



# Spectral conversion from UV to NIR Radiations by YVO<sub>4</sub>: Bi<sup>3+</sup>, Yb<sup>3+</sup> Phosphor

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## Abstract

Spectral conversion from UV to NIR in Bi<sup>3+</sup> and Yb<sup>3+</sup> ion co-doped yttrium orthovanadate (YVO<sub>4</sub>) is reported here. The material was synthesised by co-precipitation method, which provides better surface morphology. The phase of sample was characterized by X-ray powder diffraction. The spectroscopic properties were studied by NIR spectrophotometry. The characteristic NIR emission of Yb<sup>3+</sup>, owing to <sup>2</sup>F<sub>5/2</sub>-<sup>2</sup>F<sub>7/2</sub> transition was observed at 988 nm, when monitored at 340 nm, as a result of efficient energy transfer from Bi<sup>3+</sup> to Yb<sup>3+</sup> ions.

**Keywords:** Downshifting, photoluminescence (PL), energy transfer, and YVO<sub>4</sub>: Bi<sup>3+</sup>, Yb<sup>3+</sup>.

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## 1. INTRODUCTION

Sun provides huge amount of energy more than what we consume now[1]. The theoretical maximum level of efficiency for crystalline silicon (c-Si) with a energy bandgap (E<sub>g</sub>) of 1.17 eV (~ 1100 nm) is approximately 31% or 41% as defined by the Shockley-Queisser limit[2]. The luminescent materials with the quantum efficiency (QE) greater than one often called as quantum cutting phosphors could be playing a major role in the progress of lighting industry and photovoltaic technology. Ultraviolet (UV) -visible (VIS) to near-infrared (NIR) quantum cutting (QC) phosphor would be promising materials to improve the performance and conversion efficiency of solar cells. The process of QC could minimize the energy loss caused by thermalization of hot charge carriers after the absorption of high-energy photons, if the down converted photons can be absorbed by solar cells[3]. Among different lanthanum (Ln<sup>3+</sup>) ions, NIR-emitting Nd<sup>3+</sup> and Yb<sup>3+</sup> ions have attracted major attention[4-7]. Their characteristic NIR emission around 1000 nm is just above the band gap of c-Si where the solar cell shows the maximum spectral response. The NIR emissions from Yb<sup>3+</sup> ions can be effectively obtained by energy transfer (ET) from other Ln<sup>3+</sup> sensitizers [8]. The QC phosphors based on Ln<sup>3+</sup>-Yb<sup>3+</sup> (Ln = Tb, Tm, Pr, Er, Nd, Ho, and Dy) couples are still far from practical application due to low absorption cross sectional area. The dipole-allowed 4f-5d transitions have much higher absorption cross-sections[9]. Recently, attention has been paid to NIR QC by employment of Ce<sup>3+</sup>, Eu<sup>2+</sup> and Yb<sup>2+</sup> with strong absorption intensity in the ultraviolet-blue spectral region[9-10]. Bi<sup>3+</sup> ion

was found to be an efficient sensitizer for Yb<sup>3+</sup> ions[11-12].

YVO<sub>4</sub> (wakefieldite) provides favorable conditions as host material. Because of efficient resonant energy transfer from sensitizers (Bi<sup>3+</sup> ions) to lanthanide (Yb<sup>3+</sup>) ions, YVO<sub>4</sub> has been widely used as host lattice. YVO<sub>4</sub> provides favorable conditions as host material. Rambabue *et al.* reported the synthesis and PL of Bi and Yb co-doped YVO<sub>4</sub> host matrix by co-precipitation method [13]. X. Y. Huang *et al.* reported Bi, Yb doped YVO<sub>4</sub> phosphor by solid state reaction at very high temperature for long time [14].

The optimal concentration of Bi<sup>3+</sup> ions in the YVO<sub>4</sub> host matrix by co-precipitation method was found to be 3mol% (0.03mol). In this work, the method of co-precipitation had been implemented for synthesis of Y<sub>(0.97-x)</sub>VO<sub>4</sub>: 0.03Bi<sup>3+</sup>, xYb<sup>3+</sup> (x = 5mol% and 10mol%) phosphors. Co-precipitation synthesis may be regarded as an attractive method for the preparation of materials because it results in smaller grains and more homogeneous distribution of dopants ions[15-17].

## 2. EXPERIMENTAL

### 2.1 Synthesis of Phosphors

The samples of YVO<sub>4</sub> co-doped with Bi<sup>3+</sup> and Yb<sup>3+</sup> ion were prepared by co-precipitation method. The precursors Y<sub>2</sub>O<sub>3</sub> (99.9% AR), Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O (99.9% AR), Yb<sub>2</sub>O<sub>3</sub> (99.9% AR) and NH<sub>4</sub>VO<sub>4</sub> (99.9% AR) used for synthesis of Y<sub>(0.97-x)</sub>VO<sub>4</sub>: 0.03Bi<sup>3+</sup>, xYb<sup>3+</sup> (x = 5% and 10%). The composition of each chemical weighed in proper stoichiometric ratio. Y<sub>2</sub>O<sub>3</sub> (99.9% AR) and Yb<sub>2</sub>O<sub>3</sub> (99.9% AR) were heated in HNO<sub>3</sub> and

evaporated to dryness, so as to convert them into respective nitrates. The aqueous solution of all the nitrates was prepared in double distilled water and precipitated by adding aqueous solution of required quantity of  $\text{NH}_4\text{VO}_4$  (99.9% AR) drop by drop using burette. The precipitate of  $\text{Bi}^{3+}$ ,  $\text{Yb}^{3+}$  co-doped  $\text{YVO}_4$  thus formed was filtered and dried at  $80^\circ\text{C}$ . The obtained powder was crushed and heated at  $900^\circ\text{C}$  in muffle furnace for 2 h in air and quenched to room temperature..

### 2.2 Characterizations of materials

The confirmation of as prepared materials was done by XRD method using Rigaku miniflex II X-ray diffractometer with scan speed of  $2.000^\circ/\text{min}$  and  $\text{Cu K}_\alpha$  ( $\lambda = 0.15406 \text{ nm}$ ) radiation in the range  $10^\circ$  to  $80^\circ$ . The PL emission and excitation spectra were recorded at room temperature on (Hitachi F-7000) fluorescence spectrometer associated with 450W Xenon discharge lamp. The measuring parameter such as width of monochromatic slit (1.0 nm), photomultiplier tube (PMT) detector voltage, scan speed ( $240 \text{ nm}/\text{min}$ ), spectral resolution were kept constant throughout the analysis of materials. The NIR emission spectra were recorded with QM51 NIR spectrophotometer at room temperature keeping the rest of technical parameters same throughout measurements.

## 3. RESULTS AND DISCUSSION

### 3.1 XRD Analysis

The formation of the  $\text{Y}_{(0.97-x)}\text{VO}_4:0.03\text{Bi}_x\text{Yb}_x$  ( $x = 5\%$  and  $10\%$ ) samples in the crystalline phase synthesized by co-precipitation method was confirmed by XRD pattern as shown in Fig.1. The XRD pattern for  $\text{Y}_{(0.97-x)}\text{VO}_4:0.03\text{Bi}_x\text{Yb}_x$  ( $x = 5\%$  and  $10\%$ ) agreed well with the standard data from ICDD file (01-072-0274) of  $\text{YVO}_4$ . Further the XRD pattern showed that the formed material was completely crystalline and in single phase, where  $a = b = 7.1000 \text{ \AA}$  and  $c = 6.270 \text{ \AA}$ . The prepared material crystallizes in tetragonal phase and high intensity peaks observed at  $25.06$ ,  $33.68$ ,  $35.74$ ,  $49.94$ ,  $51.44$  and  $62.90^\circ$ , corresponding to plane (200), (112), (220), (312), (400) and (332) respectively. From the XRD pattern, it is inferred that the introduction of sensitizers  $\text{Bi}^{3+}$  ions activator  $\text{Yb}^{3+}$  ions did not affect the crystal structure of the  $\text{YVO}_4$  host, because  $\text{Bi}^{3+}$ ,  $\text{Yb}^{3+}$  and  $\text{Y}^{3+}$  ions have nearly similar ionic radius at appropriate approximation ( $\text{Bi}^{3+}$ :  $1.03 \text{ \AA}$ ,  $\text{Yb}^{3+}$ :  $0.86 \text{ \AA}$  and  $\text{Y}^{3+}$ :  $0.90 \text{ \AA}$ ) and hence Bi and Yb ions enter the lattice by substitution at Yttrium sites.

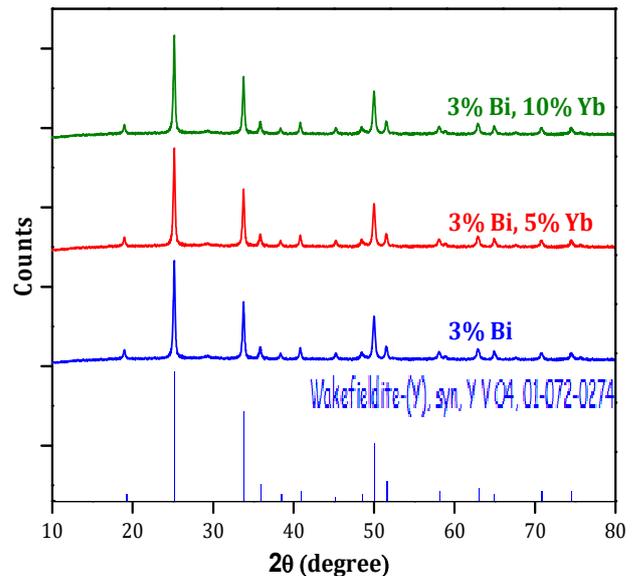


Fig. 1 XRD pattern of  $\text{Y}_{(0.97-x)}\text{VO}_4:0.03\text{Bi}_x\text{Yb}_x$  ( $x = 0\text{mol}\%$ ,  $5\text{mol}\%$  and  $10\text{mol}\%$ ) with ICDD file.

### 3.2 Photoluminescence and Energy Transfer

Fig. 2 shows the PL excitation and PL emission spectra of  $\text{YVO}_4$  co-doped with  $\text{Bi}^{3+}$  (3mol %) ions as sensitizers and  $\text{Yb}^{3+}$  ions as activators (5mol% and 10mol%) monitored at  $493 \text{ nm}$  and  $340 \text{ nm}$  respectively. The electronic configuration of  $\text{Bi}^{3+}$  ion is  $6s^2$ . Spin-orbit coupling the  $^3\text{P}_1$  and  $^1\text{P}_1$  levels of  $\text{Bi}^{3+}$  ions combine, and as a consequence,  $^1\text{S}_0-^3\text{P}_1$  and  $^1\text{S}_0-^1\text{P}_1$  transitions have reasonable absorption.  $\text{Bi}^{3+}$  ions exhibit strong absorption in the UV region of  $250-400 \text{ nm}$  through the allowed  $^1\text{S}_0-^3\text{P}_1$  transition. The broad visible emission band obtained within range  $400-600 \text{ nm}$  with the peak centered at  $493 \text{ nm}$  corresponds to  $^3\text{P}_1 \rightarrow ^1\text{S}_0$  transition of  $\text{Bi}^{3+}$  ion.

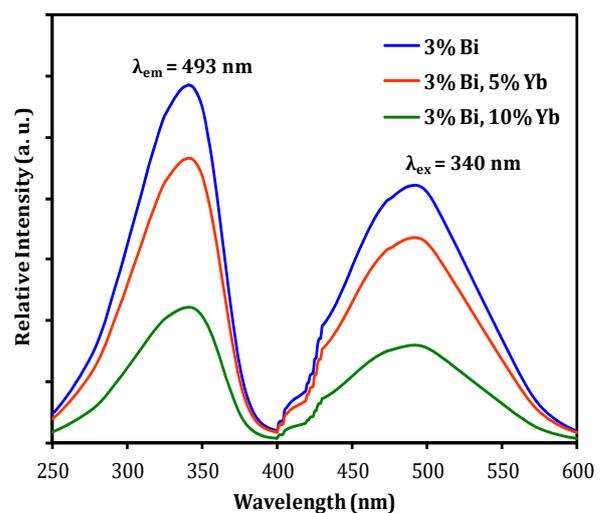


Fig.2 PL excitation and emission spectra of  $\text{Y}_{(0.97-x)}\text{VO}_4:0.03\text{Bi}_x\text{Yb}_x$  ( $x = 0\text{mol}\%$ ,  $5\text{mol}\%$  and  $10\text{mol}\%$ )



### 10mol%) recorded on F- 7000 fluorescence spectrometer

The NIR emissions from  $\text{Yb}^{3+}$  ions having peak value at 988 nm and shoulder peak at 1010 nm are monitored at 340 nm excitation wavelength as shown in Fig. 3. After a direct excitation of  $\text{Bi}^{3+}$ , an intense NIR emission band centered at 988 nm from  $\text{Yb}^{3+}$  was recorded. The excited level of  $\text{Bi}^{3+}$  ion  $^3\text{P}_1$  is situated at twice the excited energy state  $^2\text{F}_{7/2}$  of the  $\text{Yb}^{3+}$  ions and  $\text{Yb}^{3+}$  ions have no other energy levels up to the UV region. So, the ET from  $\text{Bi}^{3+}$  ions to  $\text{Yb}^{3+}$  ions takes place. After excitation  $\text{Bi}^{3+}$  ions with the 340 nm the electrons are excited to  $^3\text{P}_1$  energy level,  $\text{Bi}^{3+}$  ions obtain a wide band emission of 400 –600 nm corresponding to the  $^3\text{P}_1 \rightarrow ^1\text{S}_0$  transition of  $\text{Bi}^{3+}$  ions. Meanwhile, direct ET from  $\text{Bi}^{3+}$  ions to  $\text{Yb}^{3+}$  ion occurs and two NIR photons corresponding to  $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$  are obtained [18].

Fig.3 also showed that as  $\text{Yb}^{3+}$  ion concentration increases, the broad band visible emission due to  $\text{Bi}^{3+}$  ions is suppressed at excitation wavelength of 340 nm which is further evidence of ET from  $\text{Bi}^{3+}$  to  $\text{Yb}^{3+}$  ions. The NIR emissions due to  $\text{Yb}^{3+}$  ions are increases with concentration of  $\text{Yb}^{3+}$  ions in host matrix  $\text{YVO}_4$ .

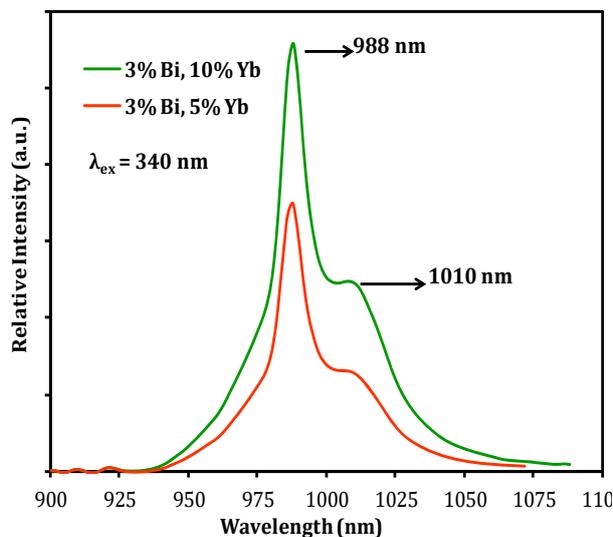


Fig.3 The NIR PL emission spectra of  $\text{Y}_{(0.97-x)}\text{VO}_4:0.03\text{Bi}, x\text{Yb}$  ( $x = 0\text{mol}\%$ ,  $5\text{mol}\%$  and  $10\text{mol}\%$ ) recorded on QM51 NIR fluorescence spectrometer

### CONCLUSION

The pure crystalline phases of  $\text{YVO}_4$  co-doped with  $\text{Bi}^{3+}$  and  $\text{Yb}^{3+}$  ions synthesized by co-precipitation method matched with ICDD file. The PL study showed the suppressed visible emission and dominant NIR emission from phosphors monitored at

340 nm wavelengths. With increase in  $\text{Yb}^{3+}$  ion concentration the ET from  $\text{Bi}^{3+}$  to  $\text{Yb}^{3+}$  increases and hence the NIR photons of wavelength 988 nm increase. where spectral response of c-Si solar cell is maximum. Our results suggest that  $\text{Bi}^{3+}$ -  $\text{Yb}^{3+}$  co-doped  $\text{YVO}_4$  phosphors are promising candidates for improving the efficiency of silicon based solar cell by means of DS process

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