



## Downconversion in $\text{YVO}_4:\text{Yb}^{3+}$ for sensitization of c-Si solar cells

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### Abstract

An efficient  $\text{Yb}^{3+}$  doped  $\text{YVO}_4$  (yttrium vanadate) material was synthesized by co-precipitation method followed by slow evaporation. The phase of phosphor was identified by X-ray diffraction (XRD) analysis. In present article the efficient near-infrared (NIR) downconversion (DC) process through energy transfer (ET) process in  $\text{YVO}_4:\text{Yb}^{3+}$  was studied. It was confirmed that there exist effective co-operative energy transfer (CET) from  $\text{VO}_4^{3-}$  ion to two neighboring  $\text{Yb}^{3+}$  ion in host matrix  $\text{YVO}_4$ . The photoluminescence (PL) of as-synthesized phosphor shows single sharp emission centered at 988 nm which corresponds to the f-f transitions in  $\text{Yb}^{3+}$  ions in  $\text{YVO}_4$  host lattice under the ultra violet (UV) excitation of 322 nm. The NIR emission of wavelength 988 nm due to  $\text{Yb}^{3+}$  was observed at the excitation of  $\text{VO}_4^{3-}$  ion, due to the CET from one  $\text{VO}_4^{3-}$  ions to two adjacent  $\text{Yb}^{3+}$  ions. The  $\text{YVO}_4:\text{Yb}^{3+}$  material can convert each UV photon into two NIR photons through CET and hence it has potential application for enhancing conversion efficiency of solar cells based on silicon materials.

**Keywords:** Energy transfer, Downconversion,  $\text{YVO}_4:\text{Yb}^{3+}$ , Solar cells.

### Introduction

Quantum cutting process (QC) via DC is able to cut one absorbed high energy photon into two minor energy photons with conversion efficiency higher than 100%<sup>1</sup>. This phenomenon can produce two low energy photons from incident high energy photons<sup>2-5</sup>. As we know that most often installed solar cells are based on c-Si have efficiency is about to 29% only<sup>6-9</sup>. However, optimum conversion efficiency 39.63% can be obtained by utilizing DC phenomenon<sup>10</sup>. The process of QC can reduce energy loss due to thermalization of hot charge carriers after the absorption of high-energy photons, if down converted photons can be absorbed by solar cells. Due to potential application in solar cells, the analysis of NIR QC phosphors has fascinated huge amount of attention in the recent years. Generally, the research work of NIR QC phosphors centered on  $\text{Re}^{3+}-\text{Yb}^{3+}$  co-doped phosphor because the transition from excited state  $^2\text{F}_{5/2}$  to  $^2\text{F}_{7/2}$  of  $\text{Yb}^{3+}$  ion give an emission corresponding to wavelength around 1000 nm, the energy slightly more than energy band gap of silicon, which can be easily captivated by c-Si solar cells. As far as the NIR radiation due to  $\text{Yb}^{3+}$  ion in  $\text{Re}^{3+}-\text{Yb}^{3+}$  co doped system is weak, because of poor absorption of the donors for their parity forbidden intra configuration 4f transitions<sup>3-12</sup>.  $\text{YVO}_4$  provide favorable conditions as host material. Due to effective and efficient resonant energy transfer (ET) from host matrix to lanthanide ions,  $\text{YVO}_4$  has been widely used as host lattice. It was established that there exist effective co-operative ET (CET) from  $\text{YVO}_4$  host matrix to activator  $\text{Yb}^{3+}$  ions<sup>3</sup>. As compare to  $\text{Re}^{3+}-\text{Yb}^{3+}$  pair, emission intensity form  $\text{Yb}^{3+}$  ions is considerably enhanced in  $\text{YVO}_4$  host having quantum efficiency (QE) 185.7%<sup>1,3</sup>. The NIR emission centered at 988 nm from  $\text{Yb}^{3+}$  ion is observed at excitation of  $\text{VO}_4^{3-}$  ion, due to CET from

one  $\text{VO}_4^{3-}$  ions to two nearest neighboring  $\text{Yb}^{3+}$  ions at a time<sup>5</sup>.

In this work the method of co-precipitation had been employed for synthesis of  $\text{YVO}_4:\text{Yb}^{3+}$ . Co-precipitation has been used to synthesize fluoride based and oxide based QC phosphor<sup>6,13-14</sup>. Co-precipitation method is effective method for the preparation of materials because it results in smaller grains and more homogeneous distribution of dopants<sup>15</sup>.

### Materials and Methods

**Synthesis of Phosphors:** The precursors  $\text{Y}_2\text{O}_3$  (Loba 99.9%),  $\text{Yb}_2\text{O}_3$  (Loba 99.9%) and  $\text{NH}_4\text{VO}_3$  (Loba 99.9%) used for synthesis of  $\text{YVO}_4:\text{Yb}^{3+}$ . The amount of each precursor was weighed in proper stoichiometric proportion. The phosphor  $\text{YVO}_4$  doped with  $\text{Yb}^{3+}$  ions with molar concentration of 1.0% was prepared by co-precipitation method. The  $\text{Y}_2\text{O}_3$  (Loba 99.9%) and  $\text{Yb}_2\text{O}_3$  (Loba 99.9%) were boiled in  $\text{HNO}_3$  and slowly evaporated to dryness, so as to convert them into respective nitrates. The aqueous solution of these nitrates was prepared in double distilled water and precipitated by adding aqueous solution of required quantity of  $\text{NH}_4\text{VO}_3$  (Loba 99.9%) drop by drop using burette. The precipitate of  $\text{Yb}^{3+}$  doped  $\text{YVO}_4$  thus formed which was filter and dried 100°C on hot plate. The obtained powder crushed by mortar pestle. The sample heated at 1000°C in muffle furnace for 2 h in air<sup>1</sup>.

**Characterizations of materials:** The confirmation of material was done by XRD analysis with the help of Rigaku Miniflex II X-ray diffractometer with scan speed of 2.000°/min and  $\text{Cu K}_\alpha$  ( $\lambda = 0.15406$  nm) radiation in the range 10° to 90°. The PL emission and PL excitation spectra were recorded with 450W Xenon discharge lamp with monochromator F-7000 FL

spectrophotometer (scan rate 240 nm/min) slit width of 1.0 nm and NIR emission spectra was recorded with QM51 NIR spectrophotometer<sup>6</sup>.

## Results and Discussion

**XRD Analysis:** The phase configuration of the  $YVO_4$  sample in crystalline form synthesized via co-precipitation technique was confirmed by XRD pattern as shown in Figure-1. The XRD pattern of  $YVO_4:Yb^{3+}$  well agreed with standard data from International Centre for Diffraction Data (ICDD) file<sup>5</sup> (01-082-1968). Additionally the XRD pattern show that the formed material was completely crystalline and in single phase. From analysis of the XRD pattern, it is understood that the introduction of activator  $Yb^{3+}$  ions does not affect the crystal structure of the  $YVO_4$  sample. Both  $Yb^{3+}$  and  $Y^{3+}$  ions have similar ionic radius at appropriate approximation ( $Yb^{3+}$ : 0.86 Å and  $Y^{3+}$ : 0.89 Å for co-ordination no. (C. N.) = 6)<sup>7</sup> and hence the ytterbium ions enters the lattice substitution ally in yttrium sites.

### Energy Transfer Mechanism and Photoluminescence

**Properties:**  $YVO_4$  host is responsible for the absorption in the spectra. It is due to excitation from filled oxygen 2p states in the valence band to the empty V 3d states of the conduction band. As there is no energy overlaps between the vanadate emission and absorption of  $Yb^{3+}$  ion and resonance between the energy of vanadate emission and the sum of the energy of excitation of two  $Yb^{3+}$  ions, we conclude that the CET from the host matrix to  $Yb^{3+}$  activators is the probable ET mechanism<sup>3</sup>. The energy

states and the mechanism of ET responsible for CET process From one  $VO_4^{3-}$  ion to two  $Yb^{3+}$  ions is shown in Figure-2. The Figure-4 showed the PL emission and PL excitation spectra of  $YVO_4:Yb^{3+}$  by using 450W Xenon discharge lamp. For  $YVO_4:Yb^{3+}$  the broad emission spectra centered at 469 nm were observed at excitation of 322 nm. In this system, upon excitation under 322 nm, a  $VO_4^{3-}$  absorbs UV photons and excited from the ground state  $VO_4^{3-}$  ion to its upper excited levels. Now, the excited electron relaxes to the lower excited levels through multi phonon nonradiative transitions. Lastly the excited electron came down to ground state emitting out blue color photons corresponding to wavelength 469 nm as shown in Figure-2 (solid greenish line). However, due to presence of  $Yb^{3+}$  ions, some of energy transferred from one excited  $VO_4^{3-}$  ion to two neighboring  $Yb^{3+}$  ions by CET process. In the meantime two near infrared photons resulting from  $Yb^{3+}: ^2F_{5/2} \rightarrow ^2F_{7/2}$  transitions were obtained approximately at same excitation wavelength as observed in PL emission spectra (Figure.3) of  $YVO_4:Yb^{3+}$  which was measured by using QM51 NIR spectrophotometer<sup>3,6</sup>.

It is observed that the emission in the IR region is occurred after the absorption of photons of wavelength 322 nm. The NIR emission band consist of two peaks, one strong peak at 988 nm and a shoulder peak at 1015 nm as shown in Figure-3. These peaks are credited to the characteristic emission from  $Yb^{3+}$ , related to transition from two distinct energy states of the  $^2F_{5/2}$  multiplet<sup>3</sup> to the lowest level of the  $^2F_{7/2}$  as shown (red dotted line) in Figure-2.

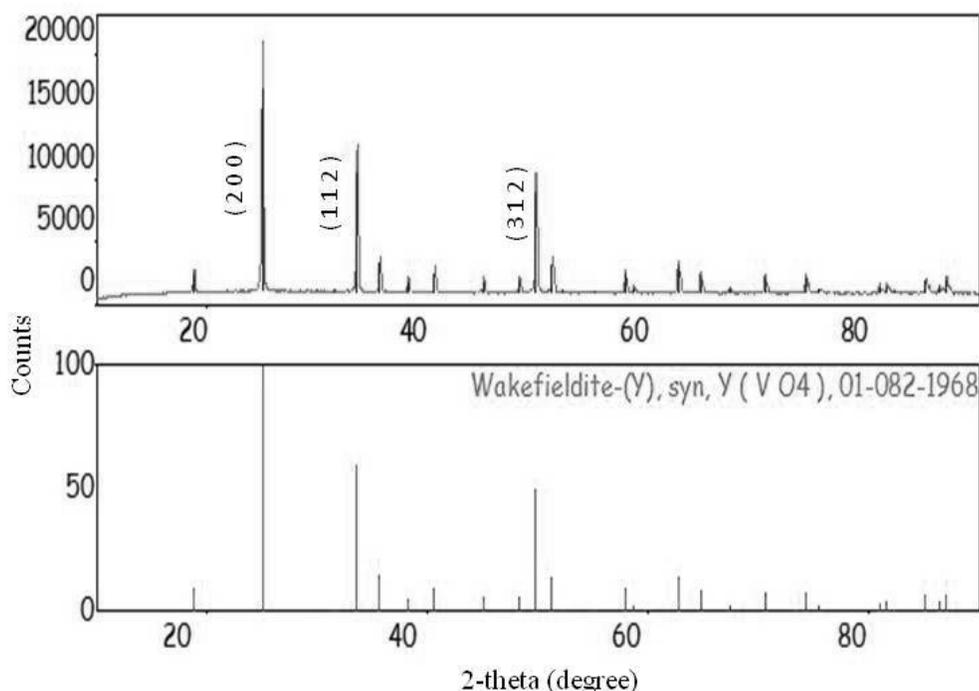
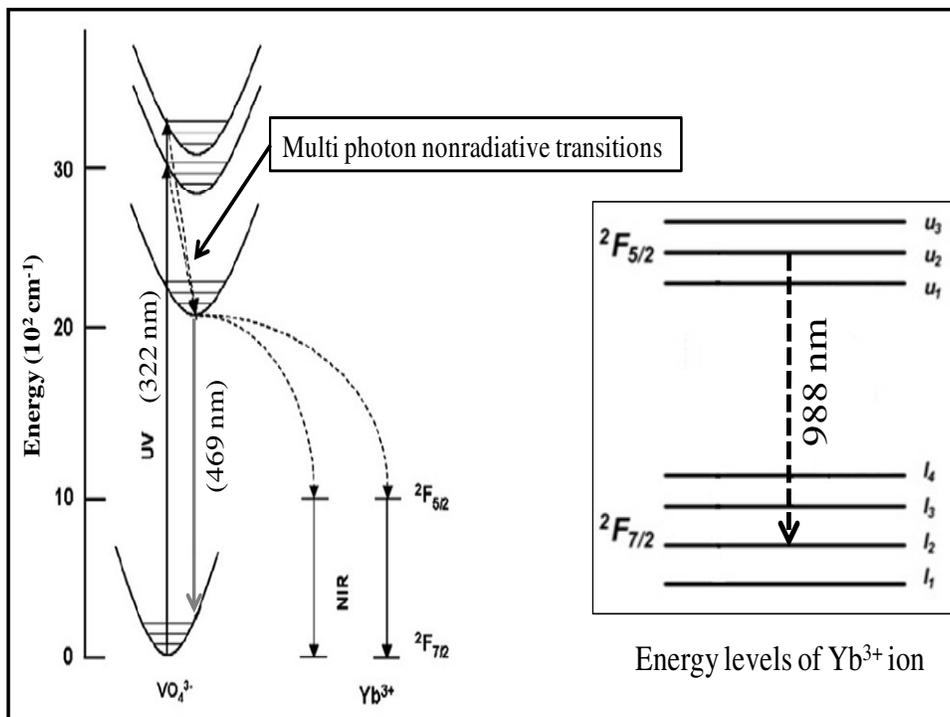
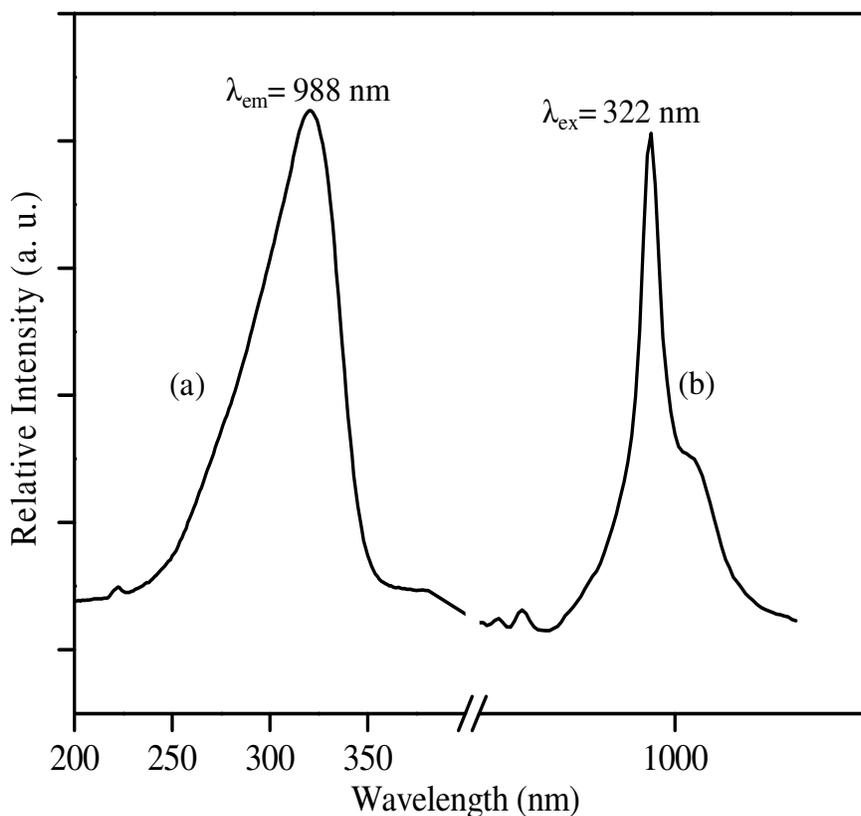


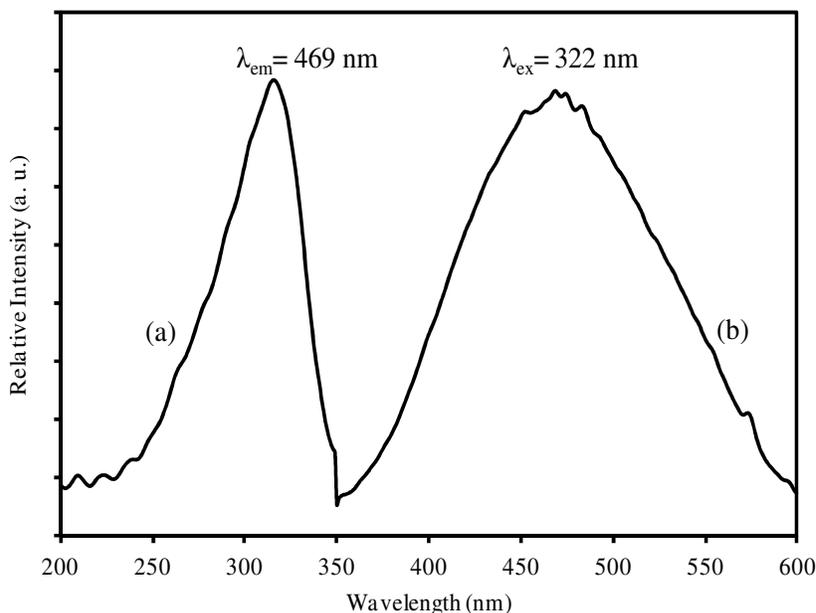
Figure-1  
XRD pattern of  $YVO_4$  doped with 1mol%  $Yb^{3+}$  ions



**Figure-2**  
 CET mechanism from VO<sub>4</sub><sup>3-</sup> to Yb<sup>3+</sup> ion in Yb<sup>3+</sup> doped YVO<sub>4</sub> material



**Figure-3**  
 Excitation (a) and NIR Emission (b) spectra of YVO<sub>4</sub> doped with 1mol% of Yb<sup>3+</sup> ion



**Figure-4**  
UV Excitation (a) and VIS Emission (b) spectra of YVO<sub>4</sub> doped with 1mol % of Yb<sup>3+</sup> ion

## Conclusion

An efficient NIR QC process was reported in prepared sample. Excitation and emission spectra measurements were done in order to establish the existence of CET between the host matrix and Yb<sup>3+</sup> ions, which lead to the 988 and 1015 nm infrared emission. However the intensity of emission the observed in NIR region (988 -1015 nm) is less than that what observed in VIS region (400-600 nm). This kind of result is expected at such low concentration of Yb<sup>3+</sup> ion in YVO<sub>4</sub> host. But at adequate (high but below the optimum value of quenching concentration) concentration of Yb<sup>3+</sup> ion much better results are expected. The application of such QC materials in combination with conventional solar cells definitely enhances conversion efficiency of solar cells. Hence play vital role to obtain clean, nonpolluting and efficient source of energy.

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