



## Spectral Downshifting in $Ce^{3+}$ - $Yb^{3+}$ co-doped $YBO_3$ phosphor

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### Abstract

*$YBO_3$  phosphor co-doped with  $Ce^{3+}$  and  $Yb^{3+}$  ions was synthesised by conventional combustion method in which ethylene diamine tetra acetic acid (EDTA) used as fuel and ammonium nitrate used as oxidizer. The prepared sample was characterized by X-ray powder diffraction (XRD) and photoluminescence (PL) properties were studied by spectrophotometers in VIS and NIR range. The blue emission (418 nm) was observed at excitation wavelength of 390 nm (UV). Further the NIR emission at 992 nm (NIR) was observed when monitored at same excitation wavelength. The material show good response towards solar spectral conversion indicating its potential application in photovoltaic (PV) technology. In this report, spectral DS from UV to NIR in  $Ce^{3+}$  and  $Yb^{3+}$  ion co-doped yttrium borate ( $YBO_3$ ) was studied.*

**Keywords:** Downshifting, c-Si solar cells, photoluminescence (PL),  $YBO_3$ :  $Ce^{3+}$ ,  $Yb^{3+}$ .

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### 1. INTRODUCTION

It has been reported that sun- light that reaches the Earth's surface provides ten thousand times more energy than what human being consume [1]. In order to utilize such tremendous source of energy, photovoltaic (PV) technology plays a very crucial role. The crystalline silicon solar cells (c-Si) are widely used for production of electricity. However the theoretical value of conversion efficiency of c-Si solar cell is 30% [2]. The major causes responsible for less efficiency of solar cell are thermalization of charge carrier and solar spectral mismatch with response of solar cell. The performance of solar cell is optimum at NIR light absorption as characteristic band gap of silicon solar cell is 1.12 eV ( $\lambda \sim 1000$  nm). Majority of photons that are present in available solar spectrum have wavelength in the range 300 nm - 600 nm.

Downshifting (DS) is a single photon luminescence process which involves conversion of one absorbed high-energy photon (UV/VIS) into one lower energy photon (NIR). This process obeys the Stokes law with wavelength change known as the Stokes shift. Though this design will not be able to overcome the Shockley-Queisser efficiency limit, as the absorption of a high energy photon by the DS phosphors can only result in the generation of one electron-hole pair in the solar cell. Luminescent DS could potentially enhance the solar cell efficiency [3]. Among various

of c-Si where the solar cell exhibits the greatest spectral response [4-7]. However, the luminescence of  $Yb^{3+}$  is relatively weak due to parity-forbidden 4f-4f transitions [8]. To solve this problem, several research groups used other luminescent species (e.g.,  $Ce^{3+}$ ,  $Bi^{3+}$ ,  $Pb^{2+}$ , and  $Cr^{3+}$ ) with higher absorption coefficients to sensitize the  $Yb^{3+}$  ions [9-16]. The  $Ce^{3+}$  ion could serve as an ideal broad band sensitizer for  $Yb^{3+}$ , because its 4f-5d transition covers a broad spectral range and, more importantly, the energy of its 4f-5d transition can be tuned by changing the crystal field strength as well as the covalency of the host [3]. The selection of host matrix is of vital importance in designing lanthanide-based luminescent phosphors for efficient PV and solar cell applications. The host materials require close lattice matches to the dopant ions and have low phonon energies.

Rare earth borates and ortho-borates normally have high ultraviolet transparency and exceptional optical damage threshold, which makes them attractive for numerous practical applications. The host  $YBO_3$  possesses wide band gap and high transparency characteristics. Hence, in recent years,  $YBO_3$  doped with different rare earth ions were discovered and studied for various applications such as fluorescent lamp, VUV absorption, and display devices. This is only because of its excellent efficiency, high color purity, very good refractory properties and good stability [17-18].

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The sample of  $\text{YBO}_3$  doped and co-doped with  $\text{Ce}^{3+}$  and  $\text{Yb}^{3+}$  ion having molar concentration of 1.0% and 3% respectively was prepared by a low cost, highly effective and time saving combustion synthesis method [19-21, 22, 23]. The precursors  $\text{Y}_2\text{O}_3$  (99.9%),  $\text{Ce}(\text{NO}_3)_3$  (99.9%),  $\text{Yb}_2\text{O}_3$  (99.9%),  $\text{H}_3\text{BO}_3$ , (99.9% AR)  $\text{NH}_4\text{NO}_3$  (99.9%) and EDTA (99.9% AR) were used for synthesis of  $\text{YBO}_3$  co-doped with  $\text{Ce}^{3+}$ - $\text{Yb}^{3+}$  ions. The composition of each chemical weighed in proper stoichiometric ratio. The precursors  $\text{Y}_2\text{O}_3$  (0.564gm, 99.9%),  $\text{Ce}(\text{NO}_3)_3$  (0.021gm, 99.9%),  $\text{Yb}_2\text{O}_3$  (0.0295gm, 99.9%),  $\text{H}_3\text{BO}_3$  (0.309gm, 99.9%),  $\text{NH}_4\text{NO}_3$  (2.801gm, 99.9%) and EDTA (2.924gm, 99.9%) were mixed together in china basin and put in resistive furnace at  $500^\circ\text{C}$ , where combustion reaction took place. The mixture melted first and gases like  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2\text{O}$  etc. were evolved. Frothing and swelling of mixture took place and then combusted with the formation of foam. The foam was gently pressed. The powder of  $\text{YBO}_3$ :  $\text{Ce}^{3+}$ ,  $\text{Yb}^{3+}$  was slowly calcinated at  $800^\circ\text{C}$  in muffle furnace for 2 h. Finally the white color phosphor in fine powder form quenched at room temperature.

The PL emission and PL excitation spectra were recorded with 450W Xenon discharge lamp associated with monochromator F-7000 FL spectrophotometer (240nm/min) with slit width of 1.0 nm wavelength range 200 nm-600 nm. The PL measurement in NIR range was carried out with FLS980 spectrophotometer. The confirmation of sample phase was done by XRD method by using Rigaku miniflex II X-ray diffractometer with scan speed of  $2.000^\circ/\text{min}$  and  $\text{Cu K}\alpha$  ( $\lambda = 0.154$  nm) radiation in the range  $10^\circ$  to  $80^\circ$ .

### 3. Results and Discussion

#### 3.1 XRD Analysis

The formation of the  $\text{YBO}_3$  in the crystalline phase prepared by combustion synthesis method was confirmed by the XRD pattern shown in Fig.1. The XRD pattern for  $\text{Y}_{0.96}\text{BO}_3:0.01\text{Ce}^{3+}, 0.03\text{Yb}^{3+}$  agreed well with the standard data from ICDD file no. 01-088-0356. The prepared phosphor  $\text{Y}_{0.96}\text{BO}_3:0.01\text{Ce}^{3+}, 0.03\text{Yb}^{3+}$  crystallize in the hexagonal phase with space group P63/m (176). The XRD also showed the prepared phosphor was completely crystalline and in single phase having lattice parameters  $a = b = 3.7760$  Å,  $c = 8.806$  Å. In the XRD pattern, high intensity peaks were observed at 34.12, 27.25, 49.90, 20.15, 48.16 and 52.71 which are corresponding to (102), (100), (104), (002) (110) and (112) planes respectively. Moreover, from analysis of the XRD pattern it is understood that the incorporation of sensitizer  $\text{Ce}^{3+}$  and activator  $\text{Yb}^{3+}$  ions didn't

influence the crystal structure of the  $\text{YBO}_3$  sample, because  $\text{Y}^{3+}$ ,  $\text{Ce}^{3+}$  and  $\text{Yb}^{3+}$  ions have similar ionic radius ( $\text{Y}^{3+}$ : 1.019Å,  $\text{Ce}^{3+}$ : 1.14 Å and  $\text{Yb}^{3+}$ : 1.009 Å) [24] and the ytterbium ( $\text{Yb}^{3+}$ ) ion enters the lattice substitutionally in yttrium sites in matrix hosts  $\text{YBO}_3$ .

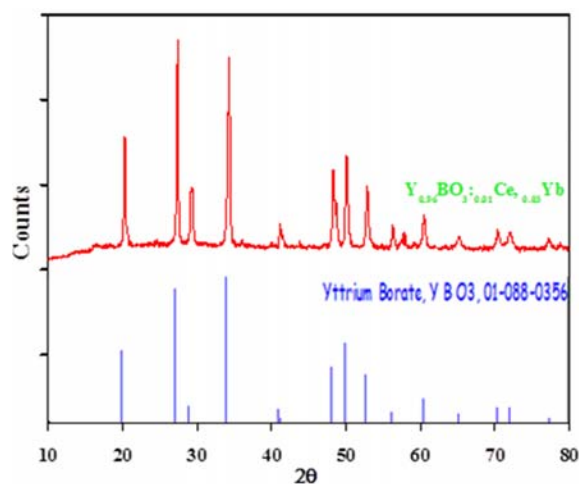


Fig.1. XRD pattern of  $\text{YBO}_3$  co-doped with  $\text{Ce}^{3+}$  and  $\text{Yb}^{3+}$  at molar conc. of 1% and 3% respectively.

#### 3.2 Photoluminescence Properties

The excitation and emission spectra of  $\text{YBO}_3$  phosphor co-doped with 1mol%  $\text{Ce}^{3+}$  and 3mol%  $\text{Yb}^{3+}$  ions is as shown in Fig.2. The excitation spectra monitored at 418 nm and emission spectra monitored at 390 nm. The blue emission at 418 nm observed which assigned to the 4f to 5d transition of  $\text{Ce}^{3+}$  ions. Fig.3 indicated that the sharp NIR emission peak observed at 992 nm (where silicon solar cell exhibits the maximum spectral response) which arises due to characteristics  ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$  transition of  $\text{Yb}^{3+}$  ions. This emission observed at same excitation wavelength of 390 nm. In host matrix  $\text{YBO}_3$ ,  $\text{Ce}^{3+}$  ions acts like sensitizer, which absorbs energy from UV (390 nm) light and transfers it to  $\text{Yb}^{3+}$  ions which act like activator and providing emission in NIR (992 nm) range. It is reported that, if  $\text{YBO}_3$  matrix solely doped with  $\text{Ce}^{3+}$  ions, then NIR emission will not be observed instead an intense blue visible emission peak observed around 414 nm [25]. We observed the same blue emission at 418 nm slightly shifted with respect to reported one. The intensity of blue emission is suppressed due to energy transfer from  $\text{Ce}^{3+}$  ion to co-doped of  $\text{Yb}^{3+}$  ions.

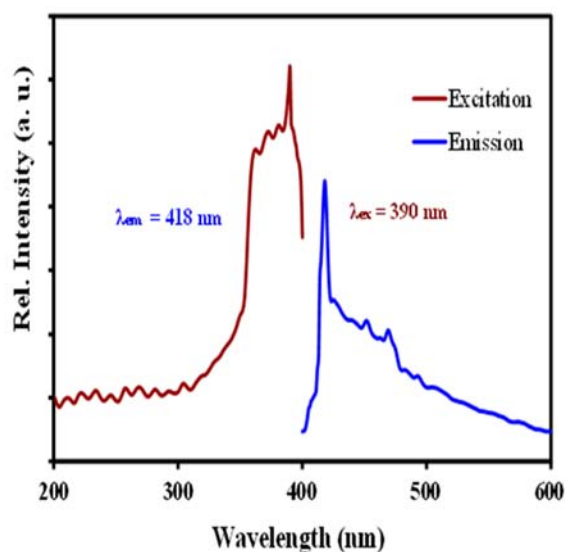


Fig.2. Excitation and Emission spectra of YBO<sub>3</sub>: Ce<sup>3+</sup>, Yb<sup>3+</sup> monitored at 418 nm and 390 nm respectively.

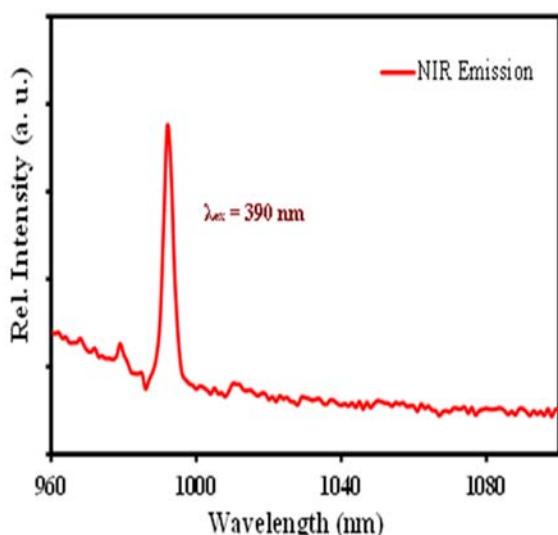


Fig3. Emission spectra of YBO<sub>3</sub>: Ce<sup>3+</sup>, Yb<sup>3+</sup> monitored at 390 nm.

#### 4. CONCLUSIONS

The pure crystalline phases of Y<sub>0.96</sub>BO<sub>3</sub>:<sub>0.01</sub>Ce<sup>3+</sup>,<sub>0.03</sub>Yb<sup>3+</sup> synthesized by combustion method is well matches with ICDD record. The DS was studied by PL spectra as UV photon in the range 360-390 nm absorbed by host due to sensitization of Ce<sup>3+</sup> ion converted into NIR photon (992 nm) where efficiency of solar cell is maximum. The blue emission occurring due to Ce<sup>3+</sup> ion can be suppressed by increasing concentration of Yb<sup>3+</sup> ions and NIR emission further increases. Our results advocated that Ce<sup>3+</sup>- Yb<sup>3+</sup> co-doped YBO<sub>3</sub> phosphors are promising

candidates for improving the efficiency of silicon based solar cell by means of DS process.

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