

An Efficient Energy Transfer in Tb^{3+} - Yb^{3+} pair co-doped Y_2O_3 Phosphors

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Abstract

The phosphor Y_2O_3 (yttrium oxide) co-doped with Tb^{3+} - Yb^{3+} ion pair had been prepared via co-precipitation route. Proper phase of material was established with X-ray diffraction (XRD) test. Also photoluminescence (PL) study was done with aid of fluorescence spectrophotometers Hitachi F7000 and FLS980 (Edinburgh photonics). In the present work the efficient energy transfer (ET) from Tb^{3+} ion to Yb^{3+} ion leading to near infra red emission (NIR) was studied in Y_2O_3 phosphor. The PL of as-synthesized phosphor shows single sharp emissions at 982 nm and 996 nm corresponding to f-f transitions of Yb^{3+} activator ions in Y_2O_3 phosphor at ultra-violet (UV) excitation wavelength of 306 nm. The dominating near IR photons emission at 982 nm from Yb^{3+} ion obtained when Tb^{3+} ion excited. Because of the ET from one Tb^{3+} sensitizer to neighboring Yb^{3+} activators suppressing emissions from Tb^{3+} ions. The $Y_2O_3:Tb^{3+}$ - Yb^{3+} phosphor can convert each UV photon into NIR photons where solar response of crystalline silicon (c-Si) solar cell is optimum. This makes the as-prepared phosphor as prime candidate for potential application in photovoltaic technology.

Keywords: Energy transfer, Downshifting, Y_2O_3 : Tb^{3+} - Yb^{3+} and Solar cells.

Introduction

The luminescence processes such as quantum cutting (QC) via downconversion (DC) which capable to split one absorbed high energy photon into two lower energy photons with quantum efficiency (QE) higher than 100% involves ET from sensitizer/s to activator/s¹. The theoretical optimum efficiency for c-Si with energy bandgap (E_g) of 1.17eV is approximately 31% or 41%, as described by Shockley–Queisser bound². The luminescence process namely QC through DC may trim down the energy defeat due to thermalization of hot charge carriers after the absorption of high energy photons after absorption of downconverted photons. Because of possible applications in PV and solar cells, the exploration of NIR DC materials has involved enormous consideration in the recent years. Generally, the research work of NIR DC phosphors focused on RE^{3+} - Yb^{3+} doped phosphor because the transition from excited state $^2F_{5/2}$ to $^2F_{7/2}$ of Yb^{3+} ions provide the emission of wavelength near about 1100 nm, the energy vaguely more than energy band gap value of silicon, which can be effortlessly absorbed by c-Si solar cells³⁻⁶. However Yb^{3+} ion cannot be excited by light within range 300-600 nm where solar response of cell is weak and host matrix such as oxides, borates and fluorides have strong absorption of UV light within 150-280 nm which is not present in terrestrial solar spectra.

Hence essentially sensitizer/s required to excite Yb^{3+} ion in host matrix. Tb^{3+} ion can play role of effective sensitizer in order to excite Yb^{3+} ion inside host matrix. The NIR QC for Tb^{3+} - Yb^{3+} co-doped systems was very first time reported by Vergeer *et al.* using YPO_4 as host matrix^{5,6}.

In this research work the co-precipitation method⁷⁻⁸ implemented for preparation of $Y_2O_3:Tb^{3+}$, Yb^{3+} phosphors. The precipitation had been used for synthesis fluoride base, chloride based and oxide base DC/QC materials. Co-precipitation method may be smart means for the synthesis of materials/phosphors since it causes smaller grains and much better homogeneous and uniform distribution of dopants in the host matrix^{6,7-9}.

Methodology

Synthesis of Materials: The co-precipitation method was used for synthesis of Tb^{3+} , Yb^{3+} co-doped Y_2O_3 phosphor. The precursor were Y_2O_3 (A.R.), Yb_2O_3 (Loba 99.9%), Tb_4O_7 (Loba 99.9%) and oxalic acid ($C_2H_2O_4$) weighed and mixed in stoichiometric proportion. The raw material Y_2O_3 was boiled with HNO_3 (A. R.) and allow to evaporat, so as to convert it into $Y(NO_3)_3$ yttrium nitrate and some double distilled water (DW) added to make homogeneous solution. The 0.05 moles of Yb_2O_3 and 0.0125 moles Tb_4O_7 in stock solutions form were added in formed $Y(NO_3)_3$ solution. An aqueous solution of oxalic acid ($C_2H_2O_4$) was added drop by drop in aqueous solution of $Y(NO_3)_3$. The precipitate of Ytterbium, Terbium doped Yttrium oxalate formed. The precipitate dried at 60°C on heating plate let allow water be slowly evaporated. The obtained materials crushed with the help of using mortal pestle and sintered at 900°C for 2hr. in air atmosphere⁸.

Characterizations of Materials: The phase confirmation of prepared materials was completed by XRD analysis using Rigaku Miniflex II X-ray diffractometer with scan speed of

2.000°/min and Cu K α ($\lambda = 0.15406$ nm) radiation in the range of 10° to 90°. The PL emission and PL excitation spectra were obtained using Hitachi F-7000 fluorescence spectrophotometer with 450W Xenon discharge lamp. The other measuring factors such as width of monochromatic slit (1.0 nm), photomultiplier tube (PMT) detector voltage, scan speed (240 nm/min), spectral resolution was kept constant during the investigation and measurements of samples. The NIR emission spectra were recorded with FLS980 (Edinburgh photonics) near IR spectrophotometer at room temperature keeping the rest of technical factors identical throughout measurements^{1,6}.

Results and Discussion

XRD Analysis: The arrangement of the Y₂O₃ material in crystalline state prepared by precipitation procedure was confirmed by XRD blueprint as shown in Figure-1. The XRD pattern of Y_{1.85}O₃·0.05Tb, 0.1Yb³⁺ well agreed with the standard data from International Centre for Diffraction Data (ICDD) file no. (01-071-0099). Moreover XRD pattern show that the formed phosphor was crystalline and in single cubic phase, where a = b

= c = 105818 Å. From analysis of the XRD pattern, it is understood that introduction of sensitizer Tb³⁺ and an activator Yb³⁺ ion do not affect crystal structure of Y₂O₃ sample, since both Yb³⁺ and Y³⁺ ions have comparable ionic radii (Tb³⁺: 1.18 Å, Yb³⁺: 0.86 Å and Y³⁺: 0.89 Å) and hence Terbium (Tb³⁺) ion and Ytterbium (Yb³⁺) ion enters the lattice site substitutionally at Yttrium (Y³⁺) sites¹⁰.

Photoluminescence Properties and Energy Transfer Mechanism:

Figure-2 and Figure-3 showed emission along with excitation spectra of prepared phosphors monitored at wavelengths 305 nm and 982 nm respectively. Figure-2 indicates that phosphor have some additional absorption band within 400-430 nm centered at 414 nm. On the other hand Figure-3 showed the strong NIR emissions peaks at 982 nm and 996 nm which are useful for solar cells applications. However there were additional peaks found at 906, 922, 961 and 1031 nm which may attribute to impurities of precursors used. These emissions are corresponding to ²F_{5/2} → ²F_{7/2} transitions in Yb³⁺ ions¹¹.

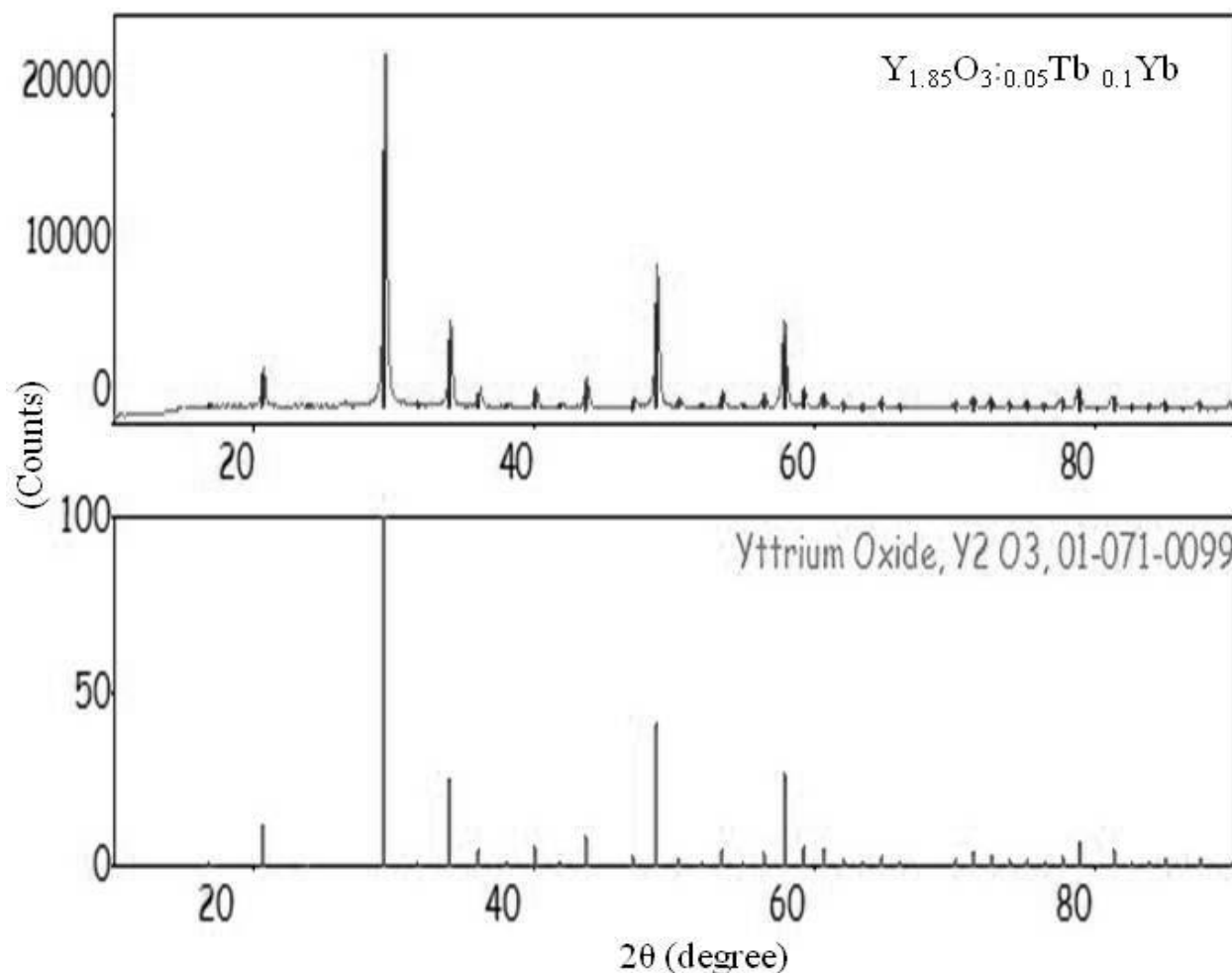


Figure-1
XRD pattern of Y₂O₃ co-doped with 0.05 mol of Tb³⁺ ion and 0.1 mol of Yb³⁺

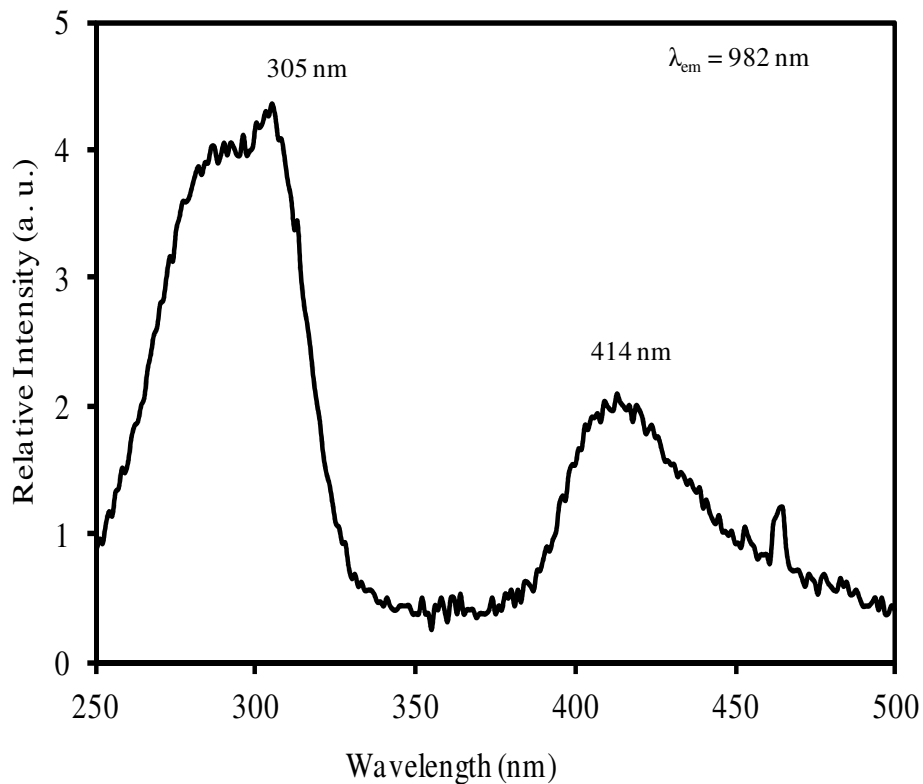


Figure-2
PL Excitation spectra of Y_2O_3 co-doped with 0.05 mol of Tb^{3+} ion and 0.1 mol of Yb^{3+}

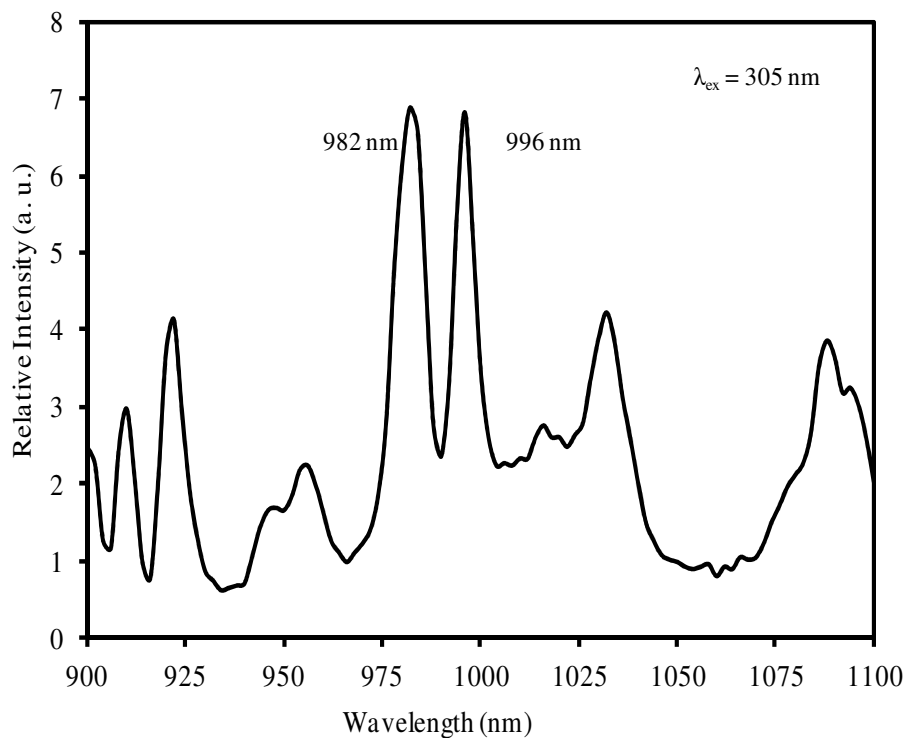


Figure-3
NIR PL Emission spectra of Y_2O_3 co-doped with 0.05 mol of Tb^{3+} ion and 0.1 mol of Yb^{3+}

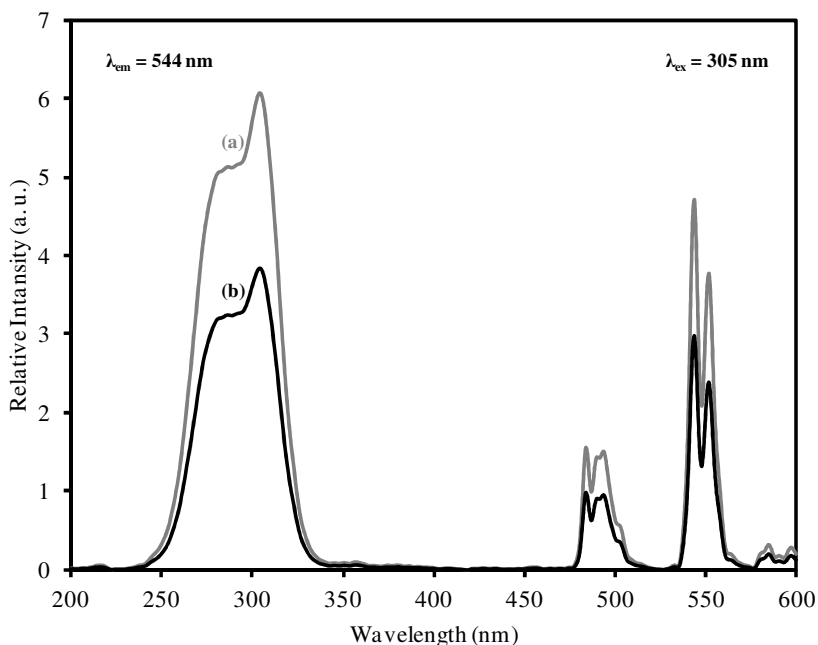


Figure-4

UV PL excitation and VIS emission spectra of (a) Y_2O_3 doped with 0.05 mol of Tb^{3+} ion and (b) Y_2O_3 co-doped with 0.05 mol of Tb^{3+} ions and 0.1 mol of Yb^{3+} ions

Figure-4(a) depicted PL emission and excitation spectra of Y_2O_3 phosphor doped with 0.05 moles of Tb^{3+} ions while Figure-4(b) showed the same for Y_2O_3 phosphor co-doped with 0.05 moles Tb^{3+} and 0.01 moles of Yb^{3+} ions. It is clearly advocating the ET from Tb^{3+} ions (sensitizers) to Yb^{3+} ions (activators). The characteristic emission of Tb^{3+} due to $^5D_4 \rightarrow ^7F_{J(6,5,4,3)}$ transitions⁹. The greenish colour emission due to $^5D_4 \rightarrow ^7F_5$ is dominating over the rest of transitions. Moreover the decrease in the green emission ($^5D_4 \rightarrow ^7F_5$) intensity of Tb^{3+} ions after addition of 0.1 moles of Yb^{3+} ions evidence that the ET from Tb^{3+} ions to Yb^{3+} ions in Y_2O_3 host matrix.

Although different Tb^{3+} - Yb^{3+} co-doped phosphors had been well studied, the issue of the primary ET mechanism from Tb^{3+} to Yb^{3+} ions is still a matter of debate¹²⁻¹⁹. For better confirmation the time decay scan of the phosphors may provide better evidences.

Conclusion

The phosphor Y_2O_3 co-doped with Tb^{3+} ions and Yb^{3+} ions was successively synthesized by precipitation process as XRD analysis indicating the phase matching. The excitation and emission spectra measurements were performed in order to prove the occurrence of ET from Tb^{3+} ions to Yb^{3+} ions, which lead to the 988 and 1015 nm infrared emissions where spectral response of c-Si solar cell is maximum. However the green emissions of Tb^{3+} ions are totally suppressed even at such high concentration (0.1 moles) of Yb^{3+} ions. At much higher concentration of Yb^{3+} ion more effective energy transfer may occur. But at the same time concentration quenching effect

cannot be neglected as it is depend on the host materials and method of synthesis. Hence by improving the synthesis technique and selecting better host, QC NIR can be obtain by ET between Tb^{3+} - Yb^{3+} ion pair. The implementation of such NIR DC phosphors in arrangement with regular PV or solar cells possibly enhances conversion efficiency of c-Si solar cells.

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