International Journal of Luminescence and Applications (ISSN: 2277-6362)
Vol. 5, No. 1, February 2015. Article ID: 064. pp.100-102.

Synthesis and Down-Conversion Studies on Y_2O_3: Yb^{3+}, Bi^{3+} Phosphor

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Abstract— *The downconverting phosphor Yb^{3+} co-doped with cubic Y_2O_3:Bi^{3+} phosphor synthesized by simple co-precipitation method. The confirmation of pure phase of Y_2O_3: Bi^{3+}, Yb^{3+} was analyzed by powder X-ray diffraction (XRD) technique. The visible–NIR PL spectra of Y_2O_3: Bi^{3+}-Yb^{3+} show near-infrared (NIR) emission around 982 nm from Yb^{3+} ($^2F_{5/2} \rightarrow {}^2F_{7/2}$) was observed under 325 nm excitation. The Co-operative energy transfer from Bi^{3+} to Yb^{3+} in Y_2O_3 host may be responsible for the downconversion emission.*

Keywords— *Co-precipitation method, Downconversion, energy transfer phenomenon, XRD, visible-NIR spectra*

PACS Code— *78.55-m*

1. INTRODUCTION

Today one of the major challenges in photovoltaic research today has to increase conversion efficiency by making better use of the solar spectrum. Considerable research recently has been focused on better exploitation of the solar cells via a photon conversion process in order to use this environmentally friendly energy source for future energy demands [1, 2, 3, 4].

The investigation of quantum cutting down conversion by cooperative energy transfer from rare earths RE^{3+} to Yb^{3+} has been a very active field of research. In this process, the absorption of one UV or blue photon can result in the emission of two Yb^{3+} ions around 980 nm. The quantum cutting phosphors based on cooperative energy transfer process could greatly benefit the development of Si-solar cells because their emission energy is just above the band gap of Si [5, 6, 7].

Recently, Wei Xian-Tao *et al.* reported that Bi^{3+} and Yb^{3+} co-doped cubic Y_2O_3 phosphors are prepared by Pechini sol–gel method. The material shows strong near-infrared (NIR) emission around 980 nm from Yb^{3+} ($^2F_{5/2} \rightarrow {}^2F_{7/2}$) is observed under ultraviolet light excitation [8].

G. Blasse *et al.* reported that, there has a luminescence quenching of a combination of this two kinds of centers from the charge transfer state $RE^{4+} - RE^{2+}$ ($Ce^{4+} - Yb^{2+}$) [9]. This effect may reduce the real quantum efficiency greatly. Thus, it has very important to find other ions without this effect. Bi^{3+} ions have $6s^2$ electronic configuration. The $6s^2 \rightarrow 6s6p$ transition is also an allowed electric-dipole transition. The emission of Bi^{3+} ions in Y_2O_3 takes place mainly around 500 nm (the energy is just twice that of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+} ions), which suggests the possibility of efficient cooperative energy transfer from Bi^{3+} to Yb^{3+}. A similarity between the ionic radii of Bi^{3+} and Y^{3+} allows for easy substitution of Bi for Y in Y_2O_3 system. It has been reported that the luminescence of Eu^{3+} or Er^{3+} can be greatly intensified with the help of resonant energy transfer from the excited Bi^{3+} ions to the Eu^{3+} or Er^{3+} ones [10, 11].

In present work, we synthesized cubic Y_2O_3 phosphor doped with Bi^{3+} and Yb^{3+} using simple co-precipitation method and studied for their PL performance.

2. EXPERIMENTAL

The Y_2O_3: Bi^{3+}, Yb^{3+} phosphor was prepared by simple co-precipitation method. The starting raw material were stoichiometric mixture of reagent grade Y_2O_3 (A.R.), Yb_2O_3 (Loba 99.9%), $Bi(NO_3)_3$ (Loba 99.9%). The raw material yttrium oxide was boiled in HNO_3 (A.R.) and evaporated to dryness, so as to convert it into respective nitrate and added 20 ml deionized water. The stock solution of Yb_2O_3 and $Bi(NO_3)_3$ were added in formed yttrium nitrate solution. The solution of oxalic acid was added drop by drop in yttrium nitrate solution. Thus the precipitation of ytterbium, bismuth doped yttrium oxalate formed. The precipitation filtered by using filter paper and dried at 80° C on heating plate. The obtained material crushed by using mortal pestle and sintered at 900°C for 2h in air atmosphere. The NIR spectra were calculated with the help of QM51 NIR spectrophotometer and the PL emission and PL excitation spectra were recorded with 450W Xenon discharge lamp associated with monochromator F-7000 FL spectrometer (240nm/min) with slit width of 1.0 nm. The confirmation of sample was done by XRD method by using Rigaku miniflex II X-ray diffractometer with scan speed of 6.000°/min and Cu Kα (λ = 1.5406 Å) radiation in the range 10° to 90°.

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3. RESULT AND DISCUSSION

3.1 XRD Analysis

The formation of the phase purity and crystal structure of Y_2O_3:Bi^{3+}, Yb^{3+} synthesized by using simple co-precipitation method sintered at 900°C was confirmed by XRD pattern as shown in Fig. 1. All the peaks in XRD pattern very well agreement with the standard data from ICDD file no. 01-071-0049. Also the XRD shows that the formed material was completely crystalline and was in single phase with cubic structure where a=b=c=10.5957 Å. The space group for Y_2O_3 is Ia-3 (206).

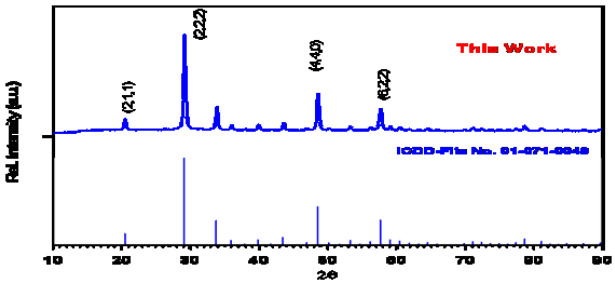

Fig. 1: XRD pattern of Y_2O_3:Bi^{3+}, Yb^{3+} phosphor.

3.2 Photoluminescence

Fig.2 shows the excitation and emission spectra of Y_2O_3:Bi^{3+} phosphor. The Bi^{3+} possesses a $6s^2$ electronic configuration, and its luminescence properties show a strong dependence on the composition and crystal structure of the host lattice. The electronic configuration of Bi^{3+} ion is composed of the ground state $^1S_0$ and four excited states $^3P_0$, $^3P_1$, $^3P_2$, and $^1P_1$ in the order of the increasing energy.

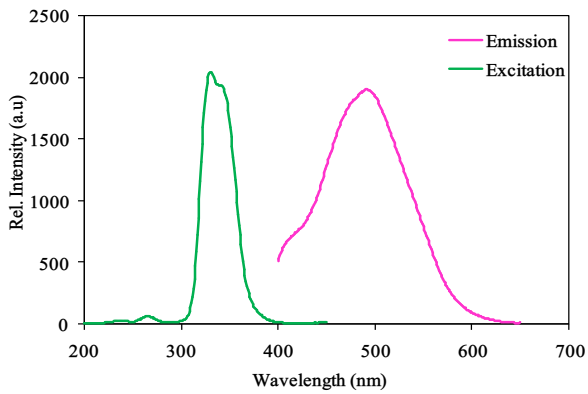

Fig. 1: Excitation and Emission spectra of Y_2O_3:Bi^{3+}

The cubic structure Y_2O_3 possesses two six-coordinated non-equivalent cation sites C_2 and S_6. Their occupancies are 75% and 25%, respectively. On the basis of intensities, Boulon [12] assigned the relatively weak emission band around 409 nm to Bi^{3+} in S_6 site, and the stronger 491 nm emission band to Bi^{3+} in C_2 site. The emission energy of Bi^{3+} in C_2 sites is just the twice that of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+} ions from this we have implying that the efficient cooperative energy transfer (CET) from Bi^{3+} to Yb^{3+} may take place.

The Y_2O_3: Bi^{3+} singly doped sample exhibits a broad band of blue fluorescence emission which extends from 400 to 500 nm when excited by 336 nm. These excitation and emission bands are assigned to the $^1S_0$-$^3P_1$ and $^3P_1$-$^1S_0$ transitions of Bi^{3+} ions, respectively.

Fig. 3 show the visible – NIR PL spectra of the Bi^{3+}–Yb^{3+} co-doped sample under the 325 nm excitation wavelength. The broad band excitation spectra of the Bi^{3+}-Yb^{3+} co-doped Y_2O_3 ranging from 230 to 360 nm, owing to the Bi^{3+} $6s^2 \rightarrow 6s6p$ transition, was monitored at 982 nm emission which corresponds to transition of Yb^{3+} i.e $^2F_{5/2} \rightarrow {}^2F_{7/2}$, which verifies the existence of energy transfer from Bi^{3+} to Yb^{3+}. In the NIR region of 930 – 1100 nm, a broad emission band peaking at 982 nm accompanied by several shoulders was observed at 996, 1032 and it can be assigned to the transitions between Stark levels of $^2F_{5/2}$ and $^2F_{7/2}$ of Yb^{3+} ions, because the Bi^{3+} ions does not give rise to NIR emission.

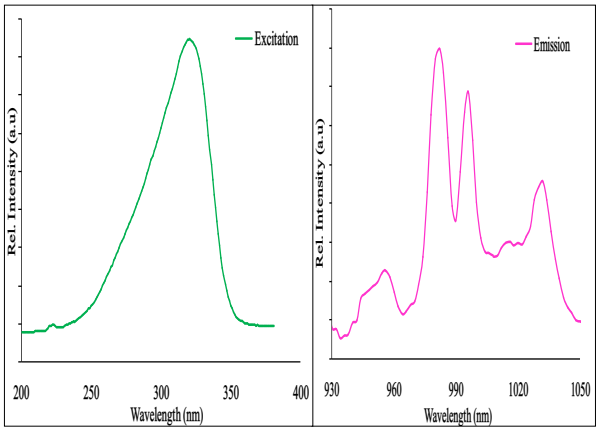

Fig. 3: Excitation and NIR emission spectra of Y_2O_3:Bi^{3+}, Yb^{3+} phosphor

The observed intense UV excited NIR emissions can only originate from the energy transfer from Bi^{3+} to Yb^{3+}. The CET of Bi^{3+}:6s6p → Yb^{3+}: $^2F_{5/2}$+Yb^{3+}: $^2F_{5/2}$ is the only possible through relaxation route to achieving the Yb^{3+} NIR emission.

Fig. 4 shows the effect of doping of Yb^{3+} ion on the emission of Y_2O_3:Bi^{3+}. The PL emission spectra of the Bi^{3+} singly doped sample under 330 nm excitation show one broad band emission in the visible range of 400–600 nm corresponding to the $^3P_1 \rightarrow {}^1S_0$ transitions of Bi^{3+}, which is consistent with the literature [13, 14, 15,]. However with the introduction of Yb^{3+} the Bi^{3+} emissions weaken, indicating the existence of the ET from Bi^{3+} to Yb^{3+} ions [16].

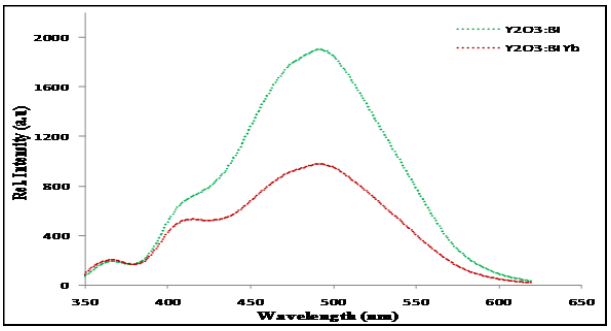

Fig. 4: Emission of Y_2O_3:Bi^{3+} and Y_2O_3 : Bi^{3+}, Yb^{3+} under the excitation of 330 nm

Fig.5. show the energy level diagrams of Bi^{3+} and Yb^{3+} ions as well as the CET process from Bi^{3+} to Yb^{3+} in the Y_2O_3 phosphor co-doped with Bi^{3+} and Yb^{3+}. In this a Bi^{3+} ion absorbs a UV photon and is excited from the ground state ($6s^2$) to the excited state (6s6p). The excited sate will relax to the ground state by emitting a blue/green photon or it can relaxes through charge energy transfer (CET) to two nearby Yb^{3+} ions because of that there is a emission in NIR region.

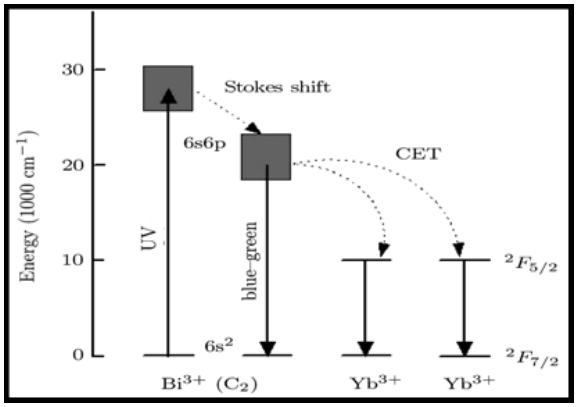

Fig. 5: Schematic energy level diagram of Bi^{3+} and Yb^{3+} ions in the Y_2O_3 phosphor

4. CONCLUSION

The downconversion phosphor of Bi^{3+}/Yb^{3+} co-doped Y_2O_3 have been successfully prepared by simple solution co-precipitation method. The phosphor possesses broad band absorption spectra in the UV region of 230 – 360 nm and exhibit NIR emission of Yb^{3+} around 982nm from corresponding transition ($^2F_{5/2} \rightarrow {}^2F_{7/2}$). In this report we notice that Bi^{3+} ion can efficiently transfer their energy to two neighboring Yb^{3+} ions by the CET process. Hence we conclude that the co-operative energy transfer (CET) from Bi^{3+} to Yb^{3+} in Y_2O_3 host is responsible for the downconversion process. The result indicate that this material has a potential application in the high efficiency silicon-based solar cells by downconversion of one UV photon, which is almost useless in the silicon solar cell to NIR photons around 982 nm where the Si solar cell exhibits the greatest spectral response.

ACKNOWLEDGEMENT

The author A. O. Chauhan is thankful to the Chairman of the FIST-DST Project at Sant Gadge Baba Amravati University, Amravati (MH), 444602 INDIA for providing XRD facility and Dr. C. P. Joshi, Department of Physics at Shri Ramdev Baba College of Engineering and Management, Nagpur (MH), 440013, INDIA for providing NIR PL characterization facility for this research work.

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