

## **Visible to Infrared Conversion in Bi-Yb and Bi-Nd Co-doped Phosphors for Si-Solar Cell**

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### **ABSTRACT**

Energy losses inherent to the conversion of sunlight to electricity in solar cells are mainly due to the so-called spectral mismatch: low energy photons are not absorbed while the energy of high energy photons is only partly used by the solar cell. The losses can be significantly reduced by adapting the solar spectrum. A promising avenue is the use of a downconversion material where *one* higher energy visible (blue-green) photon is “cut” into *two* lower-energy near-infrared photons that both can be used by the solar cell.

Due to the large number of possible valence states, strong interaction with the surrounding lattice and, in some case, cluster formation, as dopant in inorganic matrixes, bismuth ion exhibits a broad variety of optoelectronic properties and potential applications.

In this work we have successfully prepared some Bi-Yb and Bi-Nd doped phosphors. Strong NIR emission at 980 nm and 1079 nm can be ascribed to Yb and Nd respectively in the oxide lattices. The phosphors are prime candidates for quantum cutting down-conversion phosphor in Si-solar cell.

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## Introduction:

One of the major challenges in photovoltaic research today is to increase solar cell conversion efficiency [1] by making better use of the solar spectrum [2-3]. 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 [4–8]. The most popular solar cells are based on crystalline Si (c-Si) and the band gap of c-Si is about 1.12 eV ( $\sim 1100$  nm). The process of quantum cutting (QC) can convert one photon of high energy into two photons of lower energy [8]. If conversion of one incident ultraviolet (UV) or visible photon into two near-infrared (NIR) photons is realized, the main energy loss in solar cells due to the thermalization of charge carriers generated by the absorption of high-energy photons will be minimized. Fortunately, rare-earth (RE) ions with abundant energy levels are good candidates for the QC process. The research on QC systems started from single ions capable of cascade emission such as  $\text{Pr}^{3+}$  [9, 10],  $\text{Tm}^{3+}$  [11], and  $\text{Gd}^{3+}$  [12]. Then, the combination of two ions like the  $\text{Gd}^{3+}$ – $\text{Eu}^{3+}$  couple [8] through stepwise energy transfer aroused extensive attention of researchers. A QC process based on cooperative energy transfer (CET) was reported in  $\text{Yb}_x\text{Tb}_{1-x}\text{PO}_4:\text{Tb}^{3+}$  powder by Vergeer et al. [13] in 2005. Via CET, two NIR photons at 980 nm from the emission of  $\text{Yb}^{3+}$  can be obtained by the excitation of one  $\text{Tb}^{3+}$  ion with one blue photon. Since then, a similar NIR QC phenomenon has been extensively reported in RE codoped systems such as  $\text{Tb}^{3+}$ – $\text{Yb}^{3+}$  [14, 15],  $\text{Tm}^{3+}$ – $\text{Yb}^{3+}$  [16], and  $\text{Pr}^{3+}$ – $\text{Yb}^{3+}$  [17]. The single emission around 1000 nm of the  $\text{Yb}^{3+}$  ion matches well with the band gap of c-Si, so it is a good choice to realize the conversion of incident UV or visible photons into NIR photons via the QC process. However, the NIR emission of  $\text{Yb}^{3+}$  in the  $\text{RE}^{3+}/\text{Yb}^{3+}$  systems mentioned above is very weak due to the inefficient excitation of the donors for their parity-forbidden 4f–4f transitions.

$\text{Bi}^{3+}$  ion is known as efficient luminescent dopant and has been intensively studied previously in various hosts [18], including rare-earth oxides in the form of bulk material [19–20], crystalline films [21,22] or nanopowders [23].  $\text{Bi}^{3+}$  ion having commensurable ionic radius usually substitute trivalent rare-earth ions in these compounds. The ion has  $6s_2$  electronic configuration with the ground state  $^1S_0$  and four excited states  $^3P_0$ ,  $^3P_1$ ,  $^3P_2$  and  $^1P_1$ . The emission band of  $\text{Bi}^{3+}$  ion is attributed to the  $^3P_1 / ^1S_0$  transitions, the lowest absorption band is due to the  $^1S_0 / ^3P_1$  transitions [24].

It has been shown that bismuth ( $\text{Bi}^{3+}$ ) co-doping strongly enhance luminescence of lanthanide ions such as  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$  or  $\text{Er}^{3+}$  in various ionic hosts. Very recently it was shown that  $\text{Bi}^{3+}$ ,  $\text{Yb}^{3+}$ -co-doped  $\text{Y}_2\text{O}_3$  or  $\text{Gd}_2\text{O}_3$  possess efficient quantum cutting down-conversion properties due to cooperative energy transfer (CET) from  $\text{Bi}^{3+}$  to  $\text{Yb}^{3+}$  ion [25–28]. It was therefore decided to study the PL emission in  $\text{Y}_2\text{O}_3$  and  $\text{Gd}_2\text{O}_3$  and to ascertain the suitability of these phosphors for co-doping with Yb or Nd for NIR emission.

## Experimental:

Doped oxides such as  $\text{Y}_2\text{O}_3$  and  $\text{Gd}_2\text{O}_3$  were prepared by oxalate route.. Typically, 1 g  $\text{Y}_2\text{O}_3$  and 0.0178g  $\text{Yb}_2\text{O}_3$  were dissolved in  $\text{HNO}_3$  to convert into corresponding nitrates to which 0.0438g  $\text{Bi}(\text{NO}_3)_3$  was added. 1.7251 g of  $\text{H}_2\text{C}_2\text{O}_4$  was dissolved in double distilled water. The nitrate solution was added to oxalic acid solution and oxalate precipitate was obtained. The precipitate was filtered, washed and dried and was heated in a furnace for 1 hours at 900 °C. Activation with Nd was done with  $\text{Nd}_2(\text{SO}_4)_3$  converted to nitrate and the added to  $\text{Y}(\text{NO}_3)_3$ . For  $\text{Gd}_2\text{O}_3$ , starting materials were corresponding oxides or nitrates.

The samples were characterized by XRD (Rigaku miniflex), UV-VIS Spectrophotometer (Hitachi F-7000) and NIR spectrophotometer (QM-51 Photon Technology International).

## Results and Discussion:

a)  $\text{Y}_2\text{O}_3:\text{Bi}$  and  $\text{Y}_2\text{O}_3:\text{Bi, Yb}$ :

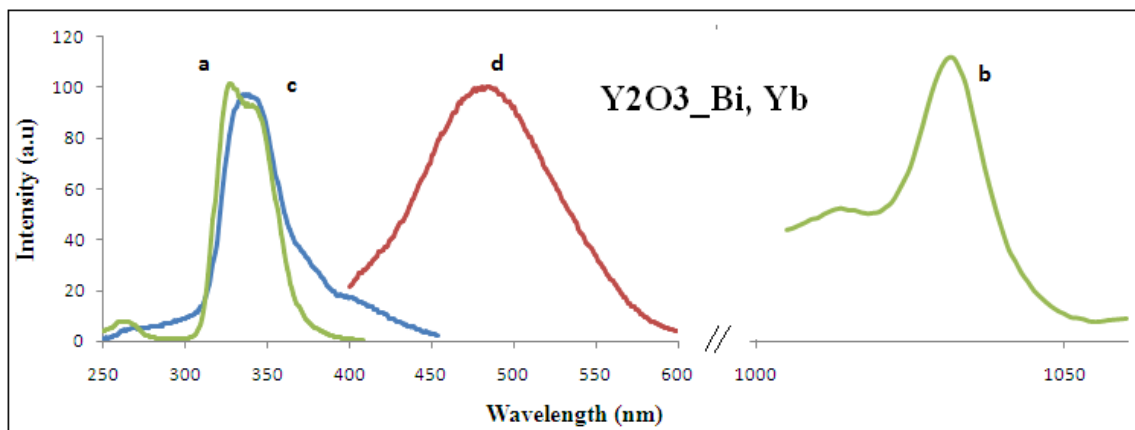


Fig 1:  $\text{Y}_2\text{O}_3:\text{Bi}$  a) Excitation in with Bi emission at 490 nm d) Emission with excitation at 327 nm in  $\text{Y}_2\text{O}_3:\text{Bi}$  c) Excitation with Yb emission at 1030 nm in  $\text{Y}_2\text{O}_3:\text{Bi, Yb}$  b) Emission with excitation at 339 nm in  $\text{Y}_2\text{O}_3:\text{Bi, Yb}$

Fig. 1 a) and d) represent the PL excitation and PLE spectrum monitoring at 330 nm and 490 nm in  $\text{Y}_2\text{O}_3:\text{Bi}$  (with 1 mole % of Bi in  $\text{Y}_2\text{O}_3$ ) respectively . The  $^3\text{P}_1$  level of  $\text{Bi}^{3+}$  [28] is split into two and three sets of energy levels under  $\text{S}_6$  and  $\text{C}_2$  symmetry [29] respectively. The green emission of  $\text{Bi}^{3+}$  490 nm) is assigned to the transition from the bottom of  $^3\text{P}_1$  to  $^1\text{S}_0$  level of  $\text{Bi}^{3+}$ . However, monitoring the green emission ( $\lambda = 492$  nm), only two bands (centered at  $\lambda = 327$  and 345 nm) can be identified in the excitation spectrum. Upon excitation of 327 or 370nm ( $\text{Bi}^{3+}$ , 1mol%,  $\text{Yb}^{3+}$ (1 mol%) consist of  $\text{Yb}^{3+}$  emission band. It is evident that the energy which  $\text{Bi}^3$  absorbed is transferred to  $\text{Yb}^{3+}$  energy levels  $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ . Also it is clear that the

excitation bands of  $Y_2O_3:Bi$  and  $Y_2O_3: Bi, Yb$  match well and hence energy transfer is observed.

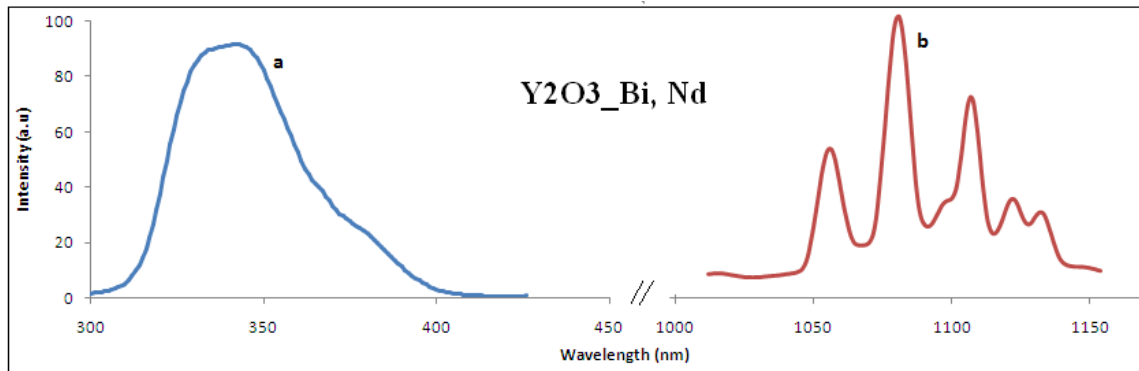


Fig 2:  $Y_2O_3:Bi, Nd$  : a) Excitation with Nd emission at 1081 nm, 1107nm, 1122 nm and 1133 nm b) Emission with excitation at 340 nm

- b)  **$Y_2O_3: Bi, Nd$** : Upon excitation of 330 nm ( $Bi^{3+}$ , 1mol%,  $Nd^{3+}$ (1 mol%)) consist of  $Nd^{3+}$  emission bands at 1081 nm, 1124 nm and 1133nm,. It is evident that the energy which  $Bi^{3+}$  absorbed is transferred to  $Nd^{3+}$  energy levels,  $^4I_{9/2,11/2,13/2}$  and intense emission is observed as shown in fig 2 b. The excitation band peaked at 330 nm have been usually ascribed to the splitting of  $Bi^{3+} \ ^3P_1 \rightarrow \ ^1S_0$  transitions. By co-doping with  $Nd^{3+}$ , As we know, silicon solar has poor spectral response in the UV and blue part of solar spectrum,  $Y_2O_3:Bi^{3+}, Nd^{3+}$  phosphor displays a broad and intense absorption band in the 300-400 nm range and can utilize the solar spectrum efficiently in the UV part and could efficiently convert the UV light into NIR light, so these materials may have the feasibility of potential application in enhancing the efficiency of c-Si solar cells.

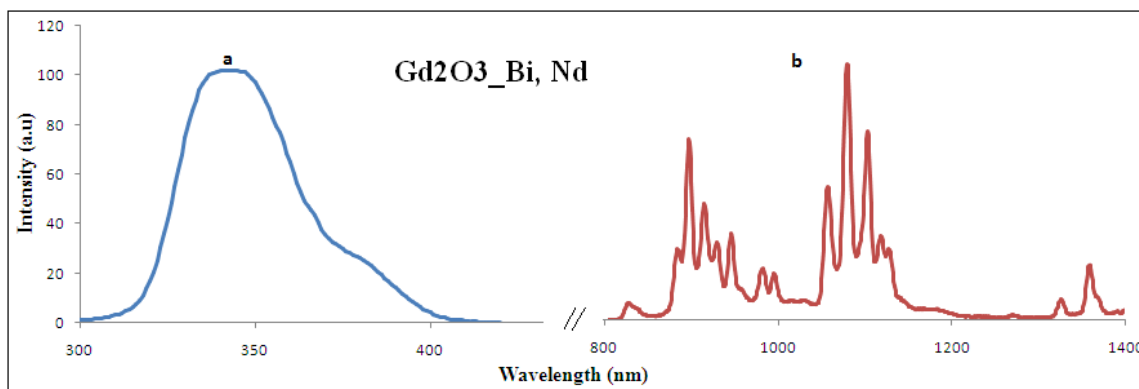


Fig 3:  $Gd_2O_3:Bi, Nd$  : a) Excitation with Nd emission at 1060nm, 1081 nm, 1107nm, 1122 nm and 1133 nm b) Emission with excitation at 340 nm

Gd<sub>2</sub>O<sub>3</sub>:Bi<sup>3+</sup>,Nd<sup>3+</sup>, gives a group of sharp emission peaks in the NIR range of 875–950 nm as shown in Fig. 3.[30] These bands are characteristic Nd<sup>3+</sup>, emissions and can be attributed to the Nd<sup>3+</sup> : <sup>4</sup>F<sub>3/2</sub>-<sup>4</sup>I<sub>9/2</sub> transition. Weak emission bands at 820 and 1060 nm corresponds to the Nd<sup>3+</sup>: <sup>4</sup>F<sub>5/2</sub>-<sup>4</sup>I<sub>9/2</sub> and Nd<sup>3+</sup>: <sup>4</sup>F<sub>3/2</sub>-<sup>4</sup>I<sub>11/2</sub> transitions can also be observed in the spectrum of Gd<sub>2</sub>O<sub>3</sub>:Bi<sup>3+</sup>,Nd<sup>3+</sup>.

It has been proposed as a good candidate for solar spectrum converter to be implicated in enhancing the photovoltaic transfer efficiency of silicon-based solar cells

## Summary

Bi<sup>3+</sup> ion is known as efficient luminescent dopant and has been intensively studied previously in various hosts. Y<sub>2</sub>O<sub>3</sub>: Bi<sup>3+</sup>, Y<sub>2</sub>O<sub>3</sub>: Bi<sup>3+</sup> Yb<sup>3+</sup>, Y<sub>2</sub>O<sub>3</sub>: Bi, Nd<sup>3+</sup> and Gd<sub>2</sub>O<sub>3</sub>:Bi<sup>3+</sup>,Nd<sup>3+</sup> were prepared by oxalate route. Intense PL emission of Bi was observed in green part of the spectrum. When co-doped with Yb or Nd corresponding emissions in NIR region was observed. Thus these phosphors can be considered as good candidates for quantum cutting.

## Acknowledgement

The authors are thankful to Department of Science and Technology, Govt of India for its funding to carry out this work.

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