Physica B xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

# Luminescence properties of $Y_2O_3$:$Bi^{3+}$, $Yb^{3+}$ co-doped phosphor for application in solar cells

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## ARTICLE INFO

*Keywords:*
Downconversion
$Y_2O_3$:$Bi^{3+}$, $Yb^{3+}$

## ABSTRACT

Bismuth ($Bi^{3+}$) and ytterbium ($Yb^{3+}$) co-doped yttrium oxide ($Y_2O_3$) phosphor powder was successfully synthesised using the co-precipitation technique. The X-ray diffraction (XRD) patterns confirmed that a single phase cubic structure with a *Ia*-3 space group was formed. The visible emission confirmed the two symmetry sites, $C_2$ and $S_6$, found in the $Y_2O_3$ host material and revealed that $Bi^{3+}$ ions preferred the $S_6$ site as seen the stronger emission intensity. The near-infrared (NIR) emission of $Yb^{3+}$ increased significantly by the presence of the $Bi^{3+}$ ions when compared to the singly doped $Y_2O_3$:$Yb^{3+}$ phosphor with the same $Yb^{3+}$ concentration. An increase in the NIR emission intensity was also observed by simply increasing the $Yb^{3+}$ concentration in the $Y_2O_3$:$Bi^{3+}$, $Yb^{3+}$ phosphor material where the intensity increased up to x = 5.0 mol% of $Yb^{3+}$ before decreasing due to concentration quenching.

## 1. Introduction

Silicon based solar cells are currently the most common form of photovoltaic cells used to convert solar energy to electrical energy. Unfortunately silicon solar cells suffer from low power conversion efficiencies, due to the mismatch between the solar spectrum and the maximum absorption spectrum of silicon [1]. In recent years, luminescent materials have been used to adapt the solar spectrum in order to reduce the spectral mismatch and improve the power conversion efficiency of the solar cells [2]. These luminescent materials have the ability of up-conversion (absorbing two or more low energy photons and converting it into one with a higher energy) or down-conversion (absorbing a high energy photon and converting it into two or more lower energy photons), in order to utilise unabsorbed photons of the solar spectrum [3,4]. Down-conversion (DC) phosphors materials doped with rare-earth elements have been used extensively in the lighting industry for potential application in mercury free fluorescent tube and plasma displays luminescent due to the wide range of possible luminescence from ultraviolet (UV) through the visible to the near-infrared (NIR) regions [5,6].

In past research, rare earth ($RE^{3+}$) – $Yb^{3+}$ (RE = Tb, Ce, Er and Pr) co-doped phosphors have been used to down-convert UV photons to NIR photons with hopes to improve the efficiency of solar cells [4]. Unfortunately lanthanides or rare-earth metals was found to be poor at absorbing photons in the UV to blue regions due to their parity forbidden 4f transition, which may cause $Yb^{3+}$ to have a weak NIR emission limiting the potential for solar cell applications [7]. Metal donors such as $Bi^{3+}$ ions have shown to be promising alternative to rare-earth ions for enhancing the NIR emission of $Yb^{3+}$ ions [6,8,9]. The $6s^2$ electron configuration of the $Bi^{3+}$ ion consists of a $^1S_0$ ground state and an excited state with a 6s6p configuration that splits into four levels, $^3P_0$, $^3P_1$, $^3P_2$, and $^1P_1$ (in order of increasing energy) [10]. Due to the $\Delta J$ selection rule the $^1S_0 \rightarrow {}^3P_0$ and $^1S_0 \rightarrow {}^3P_2$ are strongly spin forbidden, while the $^1S_0 \rightarrow {}^3P_1$ and $^1S_0 \rightarrow {}^1P_1$ are allowed transition because of the $^3P_1$ and $^1P_1$ spin-orbital coupling [5,6,9]. In this research, only the $^1S_0 \rightarrow {}^3P_1$ transition will be studied as the transition is in the region of interest, 300–400 nm [6,11].

Ytterbium ($Yb^{3+}$) is a unique rare-earth as it contains only two energy states, the $^2F_{7/2}$ ground state and $^2F_{5/2}$ excited state, separated by around 10,000 $cm^{-1}$ which translates to emission at approximately 1000 nm [12]. The NIR emission of $Yb^{3+}$ makes an ideal acceptor ion for improving the efficiency of silicon solar cells when co-doped with $Bi^{3+}$ in a $Y_2O_3$ host material due to the $^3P_1 \rightarrow {}^1S_0$ of $Bi^{3+}$ ion having twice the energy of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of $Yb^{3+}$ ions [13].

$Y_2O_3$ is an ideal host and well suited for coating solar cells due to its stable physical and chemical properties [14,15]. The host material is part of the cubic space group, 206 or *Ia*-3, where its cations are positioned in two non-equivalent Wyckoff sites, 24d with a $C_2$ symmetry and 8b with symmetry $S_6$ shown in Fig. 1 [11,14].

In this research, the luminescence properties of $Y_2O_3$:$Bi^{3+}$, $Yb^{3+}$ phosphor synthesised using the co-precipitation technique were studied and characterised for potential application in improving solar cell efficiency.

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http://dx.doi.org/10.1016/j.physb.2017.06.072
Received 10 April 2017; Received in revised form 17 June 2017; Accepted 26 June 2017
0921-4526/

Please cite this article as: Lee, E., Physica B (2017), http://dx.doi.org/10.1016/j.physb.2017.06.072

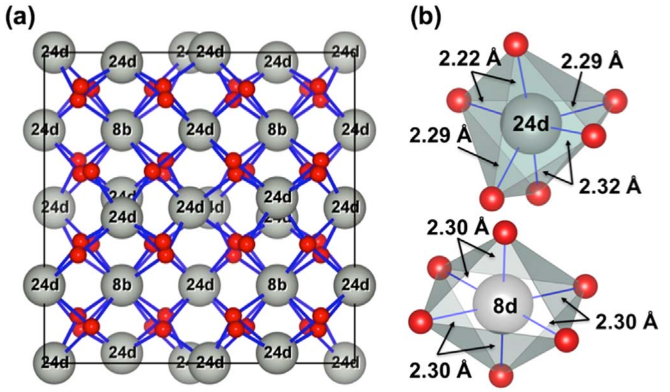

**Fig. 1.** (a) Crystal structure of $Y_2O_3$, the grey balls represent the yttrium (Y) ions situated at the 8b and 24d sites and the red balls are the oxygen (O) at the 48e ionic sites. (b) Schematic representation of the 8d and 24d sites with a polyhedral coordination in the $Y_2O_3$ host material [11]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

## 2. Experimental procedure

### 2.1. Powder synthesis

The powder samples $Y_{1.97}O_3$:$Yb_{0.03}$ and $Y_{1.98-x}O_3$:$Bi_{0.02}$, $Yb_x$ (x = 0.01, 0.02, 0.03, 0.04, 0.05 and 0.06) were synthesised using the co-precipitation technique. $Y_2O_3$ (99.99%), $Bi_2O_3$ (99.9%) and $Yb_2O_3$ (99.994%) were used as the starting materials. Stoichiometric amounts of $Y_2O_3$, $Bi_2O_3$ and $Yb_2O_3$ were placed in a beaker containing distilled water under heating and stirring. Concentrated $HNO_3$ was added dropwise to the oxide solution until the solution became clear. A $NH_4OH$ solution was added to the reaction mixture, to a pH = 10, all at once to avoid preferential precipitation. The solution containing white precipitate was stirred for 2 h. The precipitate was separated and washed using distilled water to remove excess ammonia and ammonia nitrate salt from the precipitate. The solid was placed in a drying oven heated to 100 °C until the solid was completely dry. After the drying process the solid was ground and annealed at 450 °C for 1 h then at 1000 °C for 2 h both in air to produce the final product.

### 2.2. Characterisation of $Y_2O_3$:$Bi^{3+}$, $Yb^{3+}$

Phase characterisation was obtained from the X-ray powder diffraction (XRD) patterns recorded on a Bruker D8 Advance diffractometer. The diffraction data was gathered using CuKα (1.5406 Å) X-rays at 40 kV and 40 mA, performed in air at room temperature. The ultra-violet (UV) excitation and visible emission spectra were recorded using a Varian Cary Eclipse Fluorescence spectrophotometer equipped with a xenon lamp excitation source. The near-infrared (NIR) luminescence spectrum was generated by using a Kimmon IK Series He-Cd Laser (325 nm) as the excitation source, the NIR emission was dispersed by a Horiba iHR 320 monochromator and detected by a solid state DSS-IGA020T detector.

## 3. Results and discussion

### 3.1. XRD analysis

Fig. 2 shows the XRD patterns of $Y_{1.98-x}O_3$:$Bi_{0.02}$, $Yb_x$ (x = 0.01, 0.02, 0.03, 0.04, 0.05, 0.06) powder phosphors, synthesised at pH 10 using the co-precipitation technique. The experimental XRD patterns indicated a simple cubic C-type $R_2O_3$ structure with the *Ia*-3 space group which correlate well with the referenced $Y_2O_3$ structure using the JCPDS file no.: 83-0927, which is also presented in Fig. 2. The absence of any additional diffraction patterns indicated that the addition of $Bi^{3+}$ and $Yb^{3+}$ ions did not alter the crystal structure of the $Y_2O_3$ host.

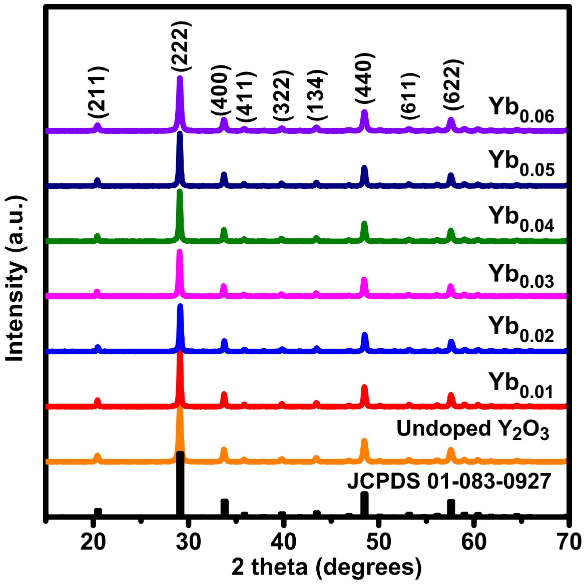

**Fig. 2.** XRD patterns of the $Y_{1.98-x}O_3$:$Bi_{0.02}$, $Yb_x$ (x = 0.01, 0.02, 0.03, 0.04, 0.05, 0.06) powder and the reference JCPDS for pure $Y_2O_3$.

Using the XRD data structural parameters namely, crystallite size and lattice constants, were investigated. The crystallite size (*D*) and micro-strain (*ε*) within the sample were calculated using the Williamson-Hall equation [16].

The lattice parameter (*a*) was determined using the formula,

$$a = \lambda\frac{\sqrt{h^2 + k^2 + l^2}}{2\sin\theta} \tag{1}$$

where (*h k l*) are the Miller indexes, *λ* is the wavelength of the radiation source and *θ* is the Bragg angle.

From the Williamson-Hall equation the crystallite size *D* was calculated by taking the inverse of the intercept gathered from the straight-line plot and similarly the micro-strain *ε* present in the samples were obtained from the slope shown in Fig. 3. The summary of all the structure parameters of the undoped $Y_2O_3$ host material and the co-doped samples are shown in Table 1.

With an increase in the $Yb^{3+}$ concentration, the lattice parameter of the prepared material decreases continuously due to the small ionic radius of $Yb^{3+}$ as compared to $Y^{3+}$ and $Bi^{3+}$ ($Yb^{3+}$, *r* = 0.087 nm; $Y^{3+}$, *r* = 0.090 nm; $Bi^{3+}$, *r* = 0.103 nm) [17]. The crystallite size was calculated to be between 27 nm and 52 nm using Williamson-Hall equation. The cause for much smaller crystallite size for the $Y_{1.97}O_3$:$Bi_{0.02}$, $Yb_{0.01}$ sample is currently still under investigation. From Williamson-Hall plot an apparent dependency of $Yb^{3+}$ concentration on the micro-strain ε, was observed due to the changes in the lattice parameter with increasing $Yb^{3+}$ concentration.

### 3.2. Photoluminescence (PL) analysis

Fig. 4(a) shows the PL excitation and emission spectrum of $Y_{1.98-x}O_3$:$Bi_{0.02}$, $Yb_x$ phosphor due to the $Bi^{3+}$ dopant. Using an excitation wavelength $\lambda_{ex}$ = 330 nm a spectrum showing a broad green emission centred at 489 nm was observed corresponding to the $C_2$ symmetry site [14]. With an excitation wavelength $\lambda_{ex}$ = 380 nm an emission band centred at 409 nm was obtained for the $S_6$ symmetry site [14]. As discussed in the literature, the excitation and emission are attributed to the $^1S_0 \rightarrow {}^3P_1$ and $^3P_1 \rightarrow {}^1S_0$ transitions of the $Bi^{3+}$ ions [8,11]. The results also revealed a variation in the luminescent intensity of the two sites, the 409 nm emission of the $S_6$ site was significantly stronger than the $C_2$ site suggesting that the $Bi^{3+}$ prefers to occupy the $S_6$ site. The preferred $S_6$ site for the $Bi^{3+}$ ions is due to its larger ionic size as compared to the $Y^{3+}$ ions and is therefore more likely to occupy