

# X-ray photoelectron spectroscopy and luminescent properties of $Y_2O_3:Bi^{3+}$ phosphor



R.M. Jafer<sup>a,b</sup>, E. Coetsee<sup>a,\*</sup>, A. Yousif<sup>a,b</sup>, R.E. Kroon<sup>a</sup>, O.M. Ntwaeaborwa<sup>a</sup>, H.C. Swart<sup>a</sup>

<sup>a</sup> Department of Physics, University of the Free State, P.O. Box 339, Bloemfontein, ZA 9300 South Africa

<sup>b</sup> Department of Physics, Faculty of Education, University of Khartoum, P.O. Box 321, Postal Code 11115 Omdurman, Sudan

## ARTICLE INFO

### Article history:

Received 23 May 2014

Received in revised form 5 December 2014

Accepted 5 January 2015

Available online 9 January 2015

### Keywords:

Cathodoluminescence

False-color CL image

X-ray photoelectron spectroscopy

$Y_2O_3:Bi^{3+}$

## ABSTRACT

X-ray photoelectron spectroscopy (XPS) results provided proof for the blue and green emission of  $Bi^{3+}$  in the  $Y_2O_3:Bi^{3+}$  phosphor. The  $Y_2O_3:Bi^{3+}$  phosphor was successfully prepared by the combustion process during the investigation of down-conversion materials for Si solar cell application. The X-ray diffraction (XRD) patterns indicated that a single-phase cubic crystal structure with the  $Ia3$  space group was formed. X-ray photoelectron spectroscopy (XPS) showed that the  $Bi^{3+}$  ion replaces the  $Y^{3+}$  ion in two different coordination sites in the  $Y_2O_3$  crystal structure. The O 1s peak shows five peaks, two which correlate with the  $O^{2-}$  ion in  $Y_2O_3$  in the two different sites, two which correlate with  $O^{2-}$  in  $Bi_2O_3$  in the two different sites and the remaining peak relates to hydroxide. The Y 3d spectrum shows two peaks for the  $Y^{3+}$  ion in the  $Y_2O_3$  structure in two different sites and the Bi 4f spectrum shows the  $Bi^{3+}$  ion in the two different sites in  $Bi_2O_3$ . The photoluminescence (PL) results showed three broad emission bands in the blue and green regions under ultraviolet excitation, which were also present for panchromatic cathodoluminescence (CL) results. These three peaks have maxima at  $\sim 3.4$ , 3.0 and 2.5 eV. The PL emission  $\sim 3.0$  eV (blue emission) showed two excitation bands centered at  $\sim 3.7$  and 3.4 eV while the PL emission at  $\sim 2.5$  eV (green emission) showed a broad excitation band from  $\sim 4$  to 3.4 eV. The panchromatic CL images were obtained for selected wavelengths at  $(2.99 \pm 0.08)$  eV (for blue emission) and  $(2.34 \pm 0.06)$  eV (for green emission). These luminescence results correlate with the XPS results that show that there are two different  $Bi^{3+}$  sites in the host lattice.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

The development of novel technologies based on nanostructured materials involves advanced microscopy and microanalysis techniques. These advanced techniques provide high sensitivity spatially resolved information about the structure, composition and properties of nanomaterials [1]. Cathodoluminescence (CL) has been widely used in laboratories since the 1980s in the assessment of optical and electronic properties of solids. This technique provides information on impurity levels and on analysis of the dopant concentration at a level that is several orders of magnitude lower than that attainable by other techniques. With the development of electron microscopy techniques, CL has emerged as an important characterization tool for the analysis of luminescent materials which properties are determined by the nature of luminescence centers (activators) doped in host crystals [2].

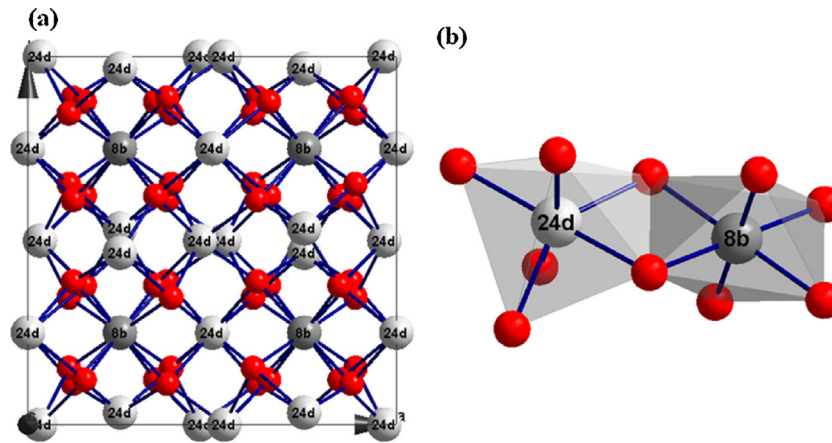
$Y_2O_3$  is an advanced ceramic host due to its stable physical and chemical properties, and this oxide is widely used as a host material in various luminescence applications [3]. This research is aimed at the investigation of the  $Y_2O_3:Bi^{3+}$  phosphor material as promising candidate for down-conversion applications in solar cells. The host belongs to the cubic C-type structure oxides where cations are distributed over two nonequivalent Wyckoff positions, namely the 8b with local symmetry  $S_6$  and 24d with local symmetry  $C_2$ .

Oxygen ions are located in the general 48e positions [4,5]. Cation site occupancy is a very important structural parameter that determines optical and other physical properties [5].

The spectroscopic and electrical properties of the  $Bi^{3+}$  ion in different hosts have attracted much attention due to its emission wavelength which varies from the ultraviolet to the red region depending on the host materials [6,7]. The similarity between the ionic radii of  $Bi^{3+}$  and  $Y^{3+}$  allows for easy substitution of the  $Bi^{3+}$  ion for  $Y^{3+}$  in the  $Y_2O_3$  system, resulting in  $Bi_2O_3$  [8]. The ground state of a free  $Bi^{3+}$  ion has a core of 78 electrons in a closed-shell state which can be regarded as inactive from the visible–UV spectroscopy point of view, while the other two active electrons are situated in

\* Corresponding author.

E-mail address: [CoetseeE@ufs.ac.za](mailto:CoetseeE@ufs.ac.za) (E. Coetsee).



**Fig. 1.** (a) The crystal structure of  $Y_2O_3$ . (The darker ball is representing the  $Y_1$  (site 8b) ionic sites and the lighter ball for the  $Y_2$  (site 24d) ionic sites. The red ball is representing O at the 48e site). (b) Schematic representation of the two different symmetry sites, namely  $Y_1$  (site 8b) and  $Y_2$  (site 24d) with their coordination polyhedra in the  $Y_2O_3$  host material. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the outer  $6s^2$  orbital. The ground state for the free  $Bi^{3+}$  ion is, therefore,  $(6s^2) ^1S_0$ , and this results in four possible excited states. Due to the spin orbit interactions, these four levels are labeled as  $^1P_0$ ,  $^3P_1$ ,  $^3P_2$  and  $^1P_1$  [8].

According to the selection rules for the total momentum of an atom ( $P_J$ ), the transitions for  $J=1$  are the strongest. Therefore, only the  $^1P_1$  and  $^3P_1$  transitions are allowed [8–10].

In this research, only the  $^1S_0 \rightarrow ^3P_1$  transition is considered because the  $Bi^{3+}$  ion absorption occurs in the range of 4.1–3.1 eV, while the transition  $^1S_0 \rightarrow ^1P_1$  is usually located at higher energies [10,11]. Furthermore, it is well known that the level  $^3P_1$  may split into sublevels due to the crystal field effect, corresponding to the position of the  $Bi^{3+}$  ion in the host. The  $^3P_1$  level considered in this work split to two ( $^3A_u$  and  $^3E_u$ ) and three ( $^3A$ ,  $^3B$  and  $^3B$ ) sublevels in the  $S_6$  and  $C_2$  symmetry sites, respectively [8,12].

Theoretical and experimental investigations were earlier produced for  $Y_2O_3$  as a host material doped with  $Bi^{3+}$  ions. Schamps et al. [8] and Real et al. [13] concluded from their theoretical results that the emission of  $Bi^{3+}$  in the  $Y_2O_3$  host is related to the occupation of  $Bi^{3+}$  ions in both the  $C_2$  and  $S_6$  sites. Boulon [14] observed two emission bands for the  $Y_2O_3:Bi^{3+}$  phosphor, namely a weak emission band at  $\sim 3$  eV which is ascribed to  $Bi^{3+}$  in the  $S_6$  site and a stronger band at  $\sim 2.5$  eV attributed to  $Bi^{3+}$  in the  $C_2$  site. According to Ju et al. [10,12], there are three emission bands centered at  $\sim 3.4$ , 3 and 2.5 eV which were assigned to the blue and green emissions for the  $Bi^{3+}$  ions occupied the  $S_6$  and  $C_2$  sites. Two luminescence emission bands have been reported in the literature for the emission of  $Y_2O_3:Bi^{3+}$  at  $\sim 3$  and 2.4 eV, which were attributed to the emission center ( $Bi^{3+}$ ) in the two cation sites ( $S_6$  and  $C_2$ ) [7,9,11,14].

To fully understand the spectroscopy of  $Bi^{3+}$  that will assist to develop new luminescent materials or applications, it is necessary to utilize any available techniques to provide additional information. This additional information is very important for the optical characterization of the emission of  $Bi^{3+}$  in the two different sites. Therefore, the XPS, panchromatic and monochromatic CL image techniques are three techniques that we used in this study to further investigate and proof the emission of  $Bi^{3+}$  in the two sites. No investigation, to the best of our knowledge, has been reported so far on XPS combined with the luminescence and on the panchromatic and monochromatic CL image results of  $Bi^{3+}$  emission in the two sites.

## 2. Experimental setup

Powder samples of  $Y_{2-x}O_3:Bi^{3+x}$  ( $x=0.002$  and  $0.03$ ) were prepared by the urea–nitrate solution combustion synthesis technique. The chemicals  $Y(NO_3)_3 \cdot 4H_2O$  (99.999%, purchased from Ma Teck GmbH Germany),  $CON_2H_4$  (99.5%) and  $Bi(NO_3)_3 \cdot 5H_2O$  (99.999%), (both purchased from Sigma Aldrich) were used as the starting materials, which were dissolved in deionized water under stirring and heating to obtain a homogenous precursor solution. The solution was placed in a furnace preheated at  $600^\circ C$ . When the combustion process was completed, the obtained solid foamy powder was ground.

The phase composition was characterized by X-ray diffraction (XRD) measurements using a BrukerD8 advance diffractometer (40 kV, 40 mA) with  $Cu K\alpha$  X-rays ( $1.54 \text{ \AA}$ ). The schematic representation of the two different symmetry sites, namely  $Y_1$  (site 8b) and  $Y_2$  (site 24d) with their coordination polyhedra in the  $Y_2O_3$  host material was drawn with the DIAMOND crystal structure software using the ICSD-16394 data file.

The PL properties were measured at room temperature using a Cary Eclipse fluorescence spectrophotometer in fluorescence mode at different excitation and emission wavelengths. X-ray photoelectron spectroscopy (XPS) was carried out with a PHI 5000 Versaprobe system. The PHI Versaprobe is driven by a patented high-flux X-ray source providing a focused monochromatic X-ray beam that can be scanned upon the sample surface. The X-ray source utilizes a focused electron beam scanned upon an Al anode for X-ray generation and a quartz crystal monochromator that focuses and scans the generated X-ray beam upon the sample surface. There is a linear relationship between the power to the X-ray anode and the resultant X-ray beam size. For example, a power of 10 W would result in a beam size of  $40 \mu m$  and 25 W, a beam size of  $100 \mu m$ . The electron gun filament is a LaB<sub>6</sub> source, the filament current is 1.5 A and the emission current is 3 mA. The control electrode is biased more negative than the filament. (Blanking voltages ranges from 0 to  $-1000$  V.) A low-energy  $Ar^+$  ion gun and low-energy neutralizer electron gun were used to minimize the sample surface charging. A  $100 \mu m$  diameter monochromatic Al  $K\alpha$  X-ray beam ( $h\nu = 1486.6$  eV) generated by a 25 W, 15 kV electron beam was used to analyze the constituent element peaks.

The pass energy was set to 11 eV giving an analyzer resolution of  $\leq 0.5$  eV. Multipack version 8.2 software was used to analyze the spectra and identify chemical elements and their electronic states using Gaussian–Lorentz fits. All the peaks were charge-referenced

Download English Version:

<https://daneshyari.com/en/article/5350603>

Download Persian Version:

<https://daneshyari.com/article/5350603>

[Daneshyari.com](https://daneshyari.com)