Journal of Nanotechnology& Advanced Materials
An International Journal

http://dx.doi.org/10.18576/jnam/050201

Synthesis and Characterizations of Rare Earth (Yb, Er) Doped Bi_2O_3 Phosphors

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Received: 30 Nov. 2016, Revised: 10Apr. 2017, Accepted: 18 Apr. 2017.
Published online: 1 July 2017.

Abstract: Bi_2O_3 phosphors doped by rare earth elements (Yb, Er) have been synthesized by precipitation method successfully. The characterizations of these phosphors have done by XRD, FTIR spectroscopy, SEM and EDAX analysis. XRD results show the presence of monoclinic phase with fine crystallinity of the materials prepared. FTIR studies show the presence of different functional groups and bonds on the surface of the phosphors. A rod like crystals formed of the synthesized material which is confirmed from SEM images. EDAX analysis shows the elemental composition of the prepared materials. It is also confirmed the presence of rare earth elements (Dopants – Yb and Er) in the host material (Bi_2O_3). NIR fluorescence study confirmed that synthesized rare earth (Yb, Er) doped Bi_2O_3 phosphors are to be liked Up-conversion phosphor.

Keywords: Phosphors, Up-conversion phosphors, Crystallinity, Dopant, NIR fluorescence.

1 Introduction

Binary oxides are materials with potential applications in many fields of study. Bismuth Oxide has been inquired extensively due to its optical and electrical properties such as refractive index, large energy band gap, dielectric permittivity as well as remarkable photoluminescence and photoconductivity [1]. Bi_2O_3 discover uses in various applications like as a catalyst and gas sensors. Compounds based on Bismuth Oxide are much better solid electrolytes than well-known stabilized Zirconia, because the FCC (face-centered cubic) Bi_2O_3 exhibits the highest ion conductivity of all oxide ion conductors [2]. There exist six polymorphs of Bismuth Oxide named: α-Bi_2O_3 (monoclinic), β-Bi_2O_3 (tetragonal), γ-Bi_2O_3 (BCC), δ-Bi_2O_3 (FCC), ω-Bi_2O_3 (orthorhombic) and ε-Bi_2O_3 (triclinic). The low temperature α-phase and high temperature δ-phase are stable, and the others are high temperature metastable phases such as β-Bi_2O_3 and γ-Bi_2O_3, these can be stabilized to exist at room temperature by doping with impurities [3, 4]. Recently, bismuth oxide has been synthesized through different such as sol-gel method [5], chemical vapor deposition [6], microwave-assisted method [7], co-precipitation method [8], etc.

Here we have introduced the up-conversion phosphors of Bi_2O_3 doped with rare earth elements (Yb and Er) synthesized by precipitation method. To the best of our knowledge there not exists any report on this type of materials. The aim of this paper is to synthesize bismuth oxide phosphors doped with rare earth elements and study of characteristics of this prepared materials by different characterization techniques.

2 Materials and Methods

2.1 Materials

Bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$ – 98% Sigma-Aldrich), Ytterbium nitrate pentahydrate ($Yb(NO_3)_3{\cdot}5H_2O$ - 99.9% Sigma-Aldrich), Erbium nitrate pentahydrate ($Er(NO_3)_3{\cdot}5H_2O$ – 99.9% Sigma-Aldrich), Nitric Acid (HNO_3 – Fisher Scientific), PEG 400 (Loba-Chemie), Sodium Hydroxide (NaOH – Fisher Scientific), Absolute alcohol (Fisher Scientific) and DI water. All reagents used in this study were of analytical grade and were used without further

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purification. Here we were used three different concentration of **Bi:Yb:Er** as (i) 79:20:1 (ii) 78:20:2 and 77:20:3 labeled them with **BO 1, BO 2 and BO 3** respectively.

2.2 Preparation of Bismuth Oxide phosphors doped with Yb and Er

Bi_2O_3 phosphors doped with Yb and Er was prepared by precipitation method. The method was illustrated in the form of flow chart as shown below:

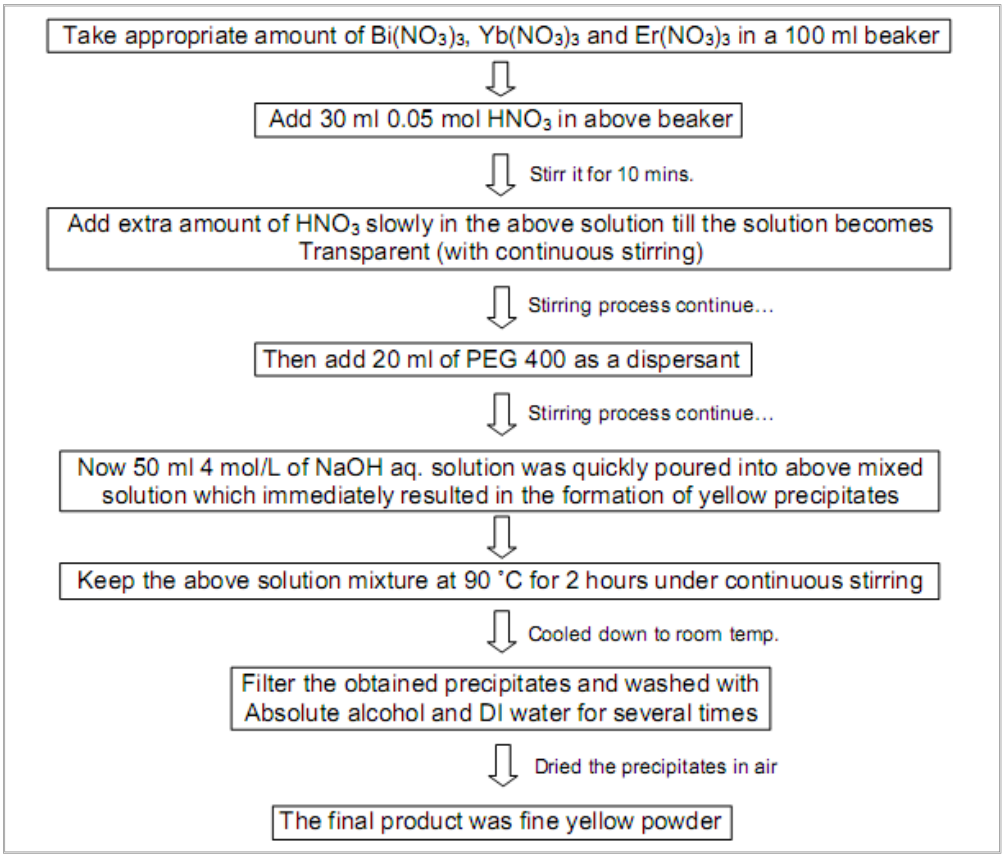

Chart 1

3 Characterizations

The prepared phosphors were characterized by the following method:

(i) XRD analysis: The powder X-ray diffraction (XRD) patterns were recorded on a X'Pert Pro PANalytical powder diffractometer with Cu-Kα radiation source (λ = 1.54 Å) operated at 40 kV and 40 mA in the 2Θ range 20 - 80º at the scan speed of 0.05º per second.

(ii) FTIR spectroscopy: Fourier transform infrared spectra were recorded with a SHIMADZU FTIR – 8400S spectrometer over the wave number range of 4000 – 400 cm^{-1}. The spectra of prepared samples were taken using KBr disks.

SEM and EDAX analysis: SEM images of the prepared materials were recorded with a JEOL make MODEL JSM 5810 LV and the quantitative elemental composition analysis was carried out by energy dispersive X – ray spectroscopy (EDAX) system with the same SEM Machine.

4 Results

4.1 XRD Analysis

Figure 4.1 (a), (b) and (c) shows the X-ray Diffraction patterns of the as prepared Bi2O3 phosphors doped with Yb and Er with different concentration as denoted by BO 1, BO 2 and BO 3.

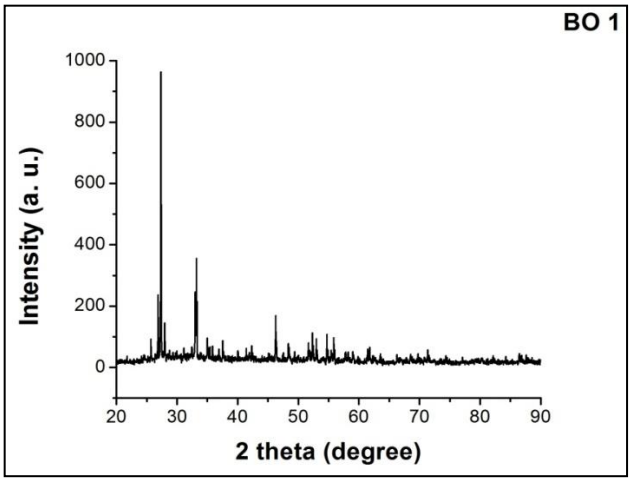

Figure 4.1(a): XRD patterns of as-prepared Bi2O3 phosphors doped with Yb and Er (BO 1)

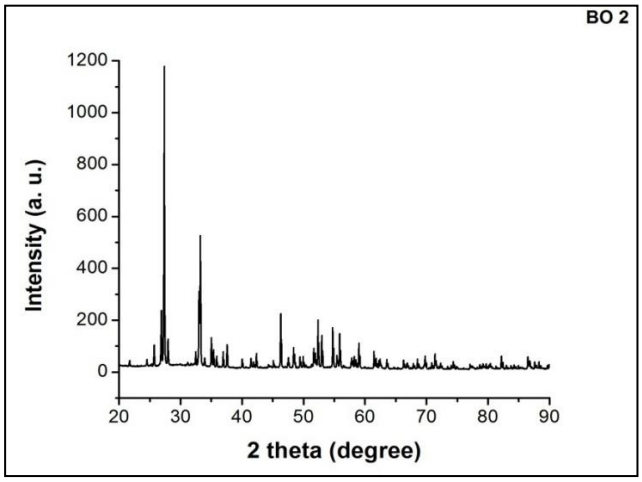

Figure 4.1(b): XRD patterns of as-prepared Bi2O3 phosphors doped with Yb and Er (BO 2)

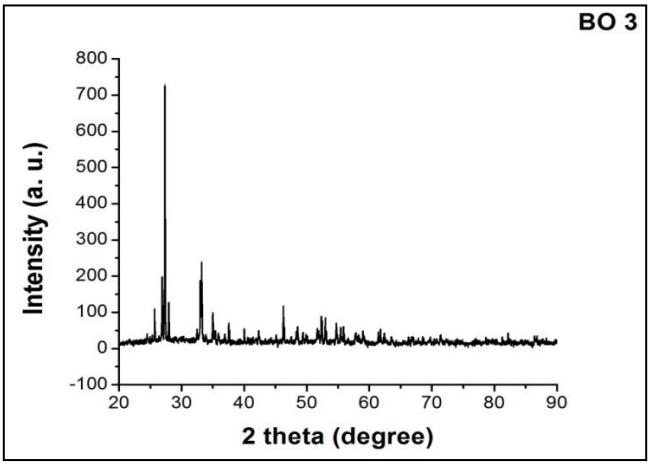

Figure 4.1(c): XRD patterns of as-prepared Bi2O3 phosphors doped with Yb and Er (BO 3)

Figure 4.1 (a), (b) and (c) shows the sharp and intense peaks of Bi_2O_3 phosphors. Features of all these three patterns indicate the presence of Monoclinic (α-Bi_2O_3) phase. It is confirmed with JCPDS file (JCPDS: 71 – 2274). The sharp diffraction peaks confirm the high crystallinity of the synthesized materials. Table 4.1 shows the average crystallite size of BO 1, BO 2 and BO 3 were calculated from Debye - Scherer's equation.

Table 4.1: Doping concentration and Crystallite size of BO 1, BO 2 and BO 3

Concentration of Doped rare-earth elements (Bi:Yb:Er)	Crystallite Size (nm)
BO 1 (79:20:1)	138.54
BO 2 (78:20:2)	110.70
BO 3 (77:20:3)	100.75

It is clear from the table 4.1 that with increase in concentration of Er in the host material (Bi_2O_3), the average crystallite size decreases.

4.2 FTIR Spectroscopy

FTIR spectrum was measured to analyze the structural properties and bond of Bi_2O_3: Yb, Er phosphors. The FTIR spectra of the as-prepared BO 1, BO 2 and BO 3 are shown in the figure 3.2 (a), (b) and (c).

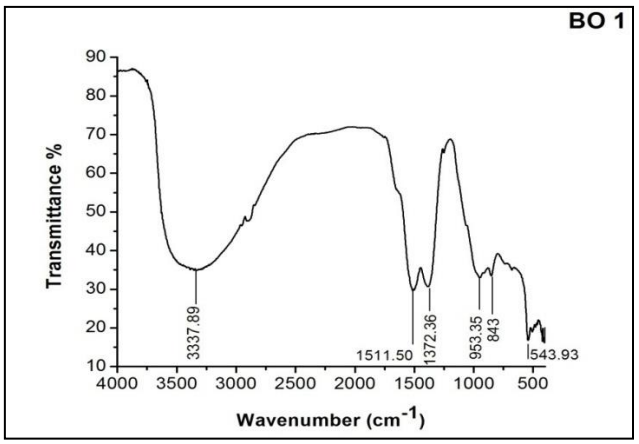

Figure 4.2 (a): FTIR spectra of the as prepared BO 1

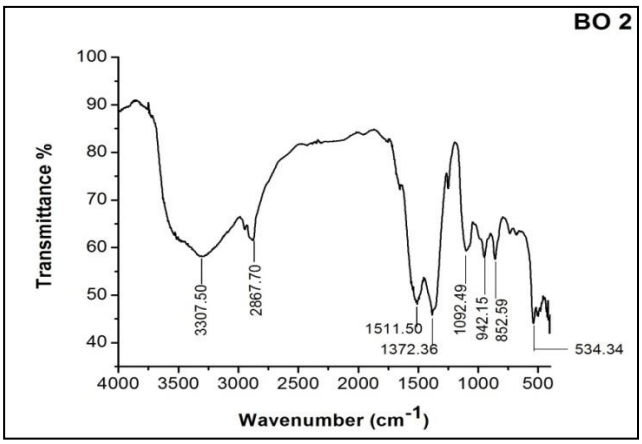

Figure 4.2 (b): FTIR spectra of the as prepared BO 2

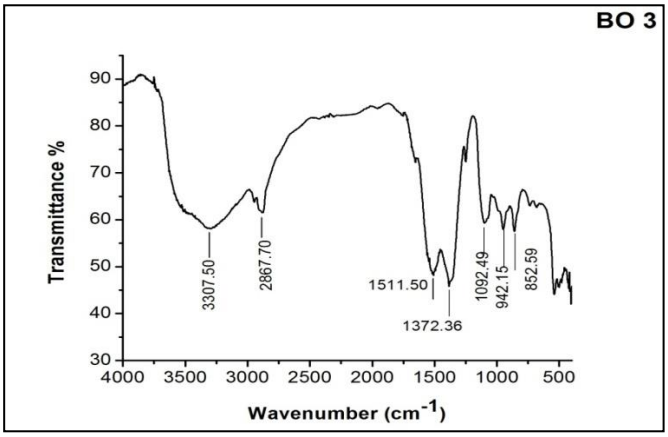

Figure 4.2 (c): FTIR spectra of the as prepared BO 3

Table 4.2: The detailed information about characteristics of the materials and information about the presence of various bonds in the synthesized materials.

Observed frequency Band (cm^{-1})	Standard frequency Band (cm^{-1})	Intensity	Group & Class	Assignment & Remarks
3337.89	3420 – 3250	S	-OH in alcohols & phenols	OH stretch (solids & liquids)
3307.50				
1511.10	1550 – 1490	S	NO_2 in aromatic nitro compounds	NO_2 antisym stretch
1372.36	1375 – 1350	S	NO_2 in aliphatic nitro compounds	NO_2symstrech
1092.49	1120 – 1080	S	C – O – H in secondary or tertiary alcohols	C – O stretch
953.35	1030 – 950	W	Carbon ring in cyclic compounds	Ring breathing mode; strong in Raman
942.15	950 – 900	Vs	$CH=CH_2$ in vinyl compounds	CH_2 out of plane wag
852.59	860 – 760	Vs (br)	R – NH_2 primary amines	NH_2 wag
843				
543.93	580 – 520	M	NO2 in aromatic nitro compounds	NO2 deformation

(S= strong, Vs=Very strong, Vs (br)=Very strong but broad, W= wide, M=medium)

4.3 SEM Images

SEM images give surface topography of the materials. It also gives size of the prepared materials. Figure 4.3 (a), (b) and (c) shows the SEM images of the BO1, BO 2 and BO 3 with 1000x and 2000x magnification respectively. It is clear from all images that a rod like crystals were formed in the synthesized materials. Size of prepared materials varies between 10 to 15 microns.

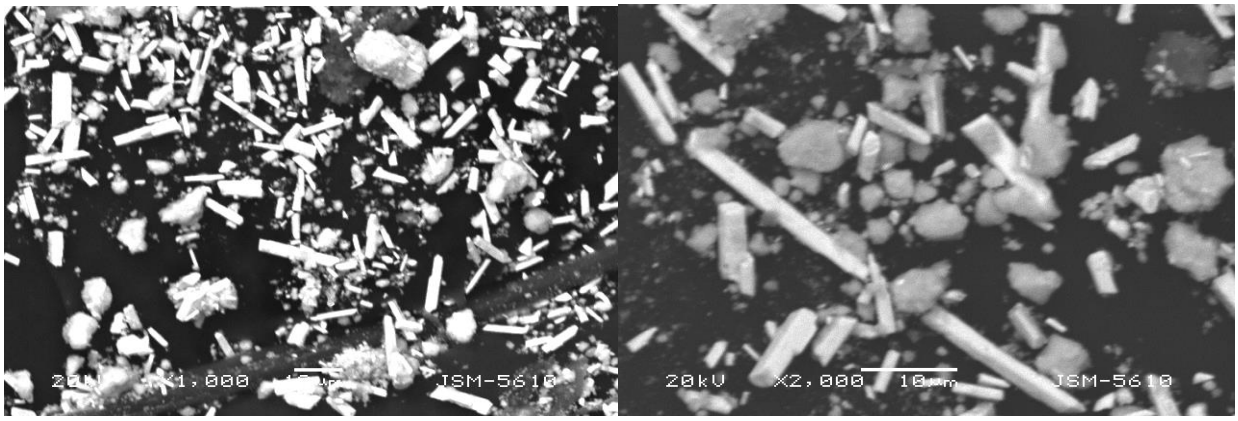

Figure 4.3 (a): SEM images of as BO 1 at 1000X and 2000X

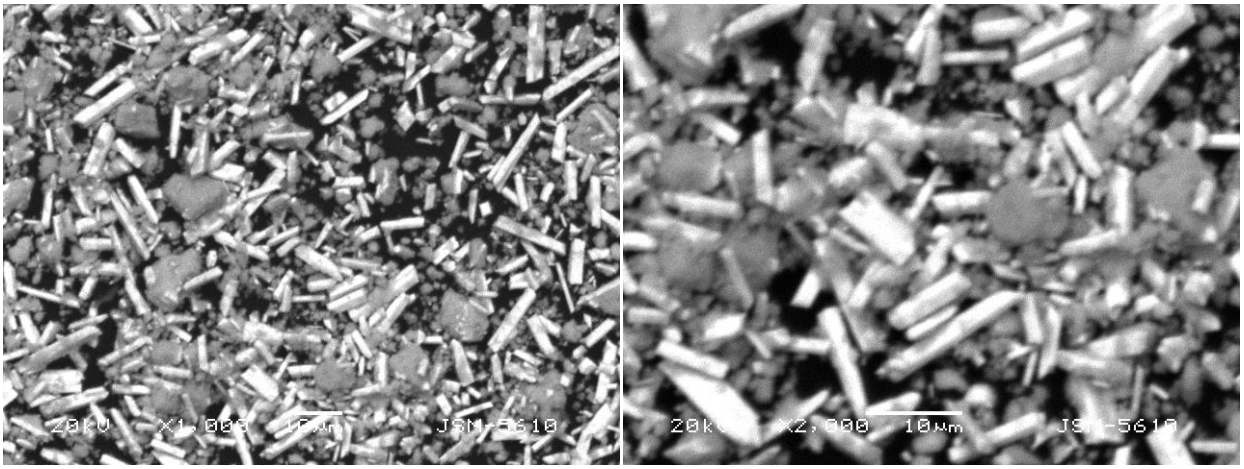

Figure 4.3 (b): SEM images of as BO 2 at 1000X and 2000X

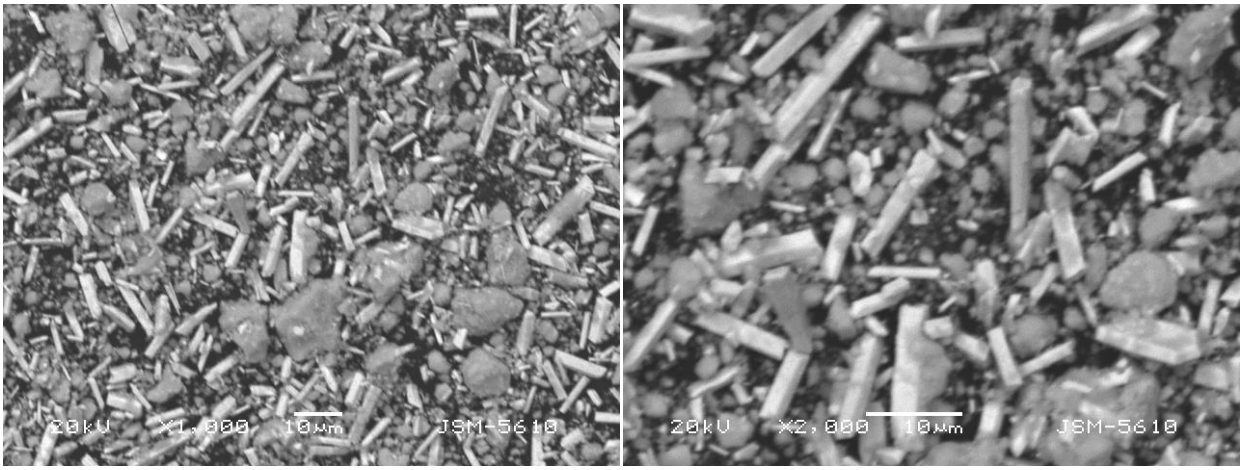

Figure 4.3 (c): SEM images of as BO 3 at 1000X and 2000X

4.4 EDAX analysis

The elemental composition analysis of the rare earth doped Bi2O3 up-conversion phosphor has been carried out using EDAX. Figure 4.4 (a), (b) and (c) shows the EDAX spectra of BO 1, BO 2 and BO 3 respectively.

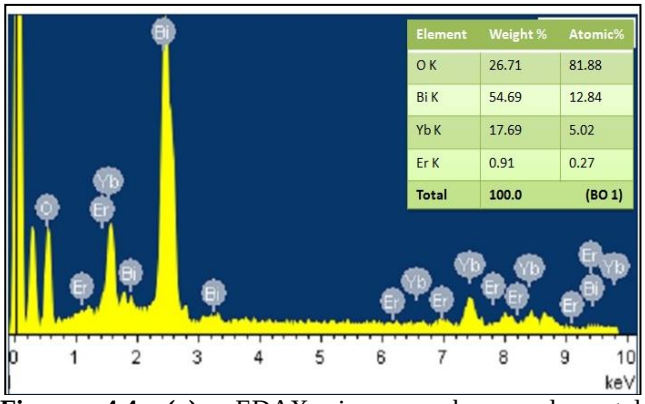

Figure 4.4 (a): EDAX images shows elemental composition of BO 1

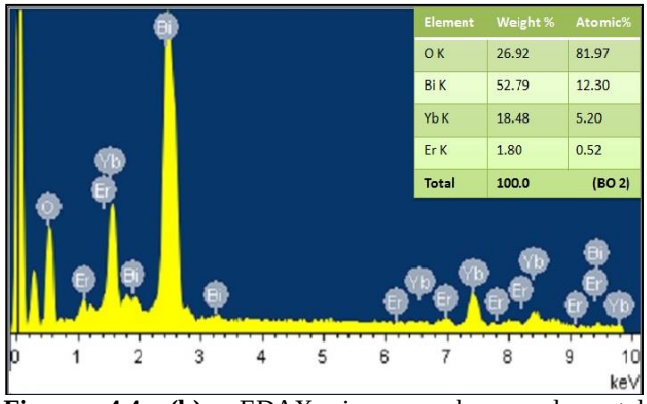

Figure 4.4 (b): EDAX images shows elemental composition of BO 2

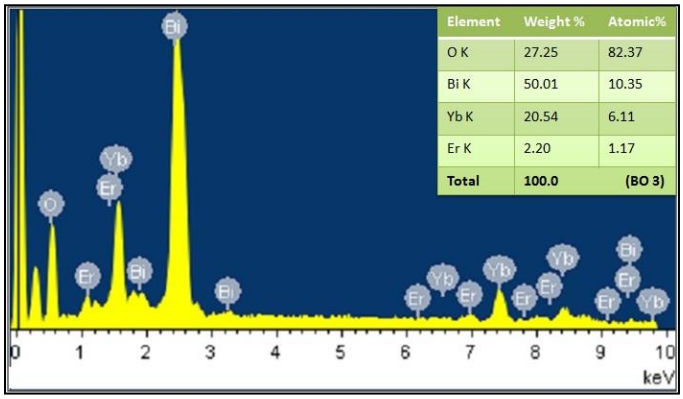

Figure 4.4 (c): EDAX images shows elemental composition of BO 3

Peaks at about 1, 1.6, and 6.2 to 9.8 keV confirm the doping of rare earth elements (Yb and Er) into host material Bi_2O_3.

4.5 NIR Fluorescence

Fluorescence study has carried out using a NIR Laser diode pen as shown in the figure 4.5 (a). Up-conversion Phosphors means that material in which two or more photons followed by excitation at 980 nm gives emission in the visible region. Upon the excitation at 980 nm wavelength, the prepared up-conversion phosphors (**(Yb, Er) doped Bi_2O_3 Phosphors**) gives emission in the visible region (Green Color) as shown in the figure 4.5 (b).

Figure 4.5 (a): NIR Laser Diode Pen (980 nm)

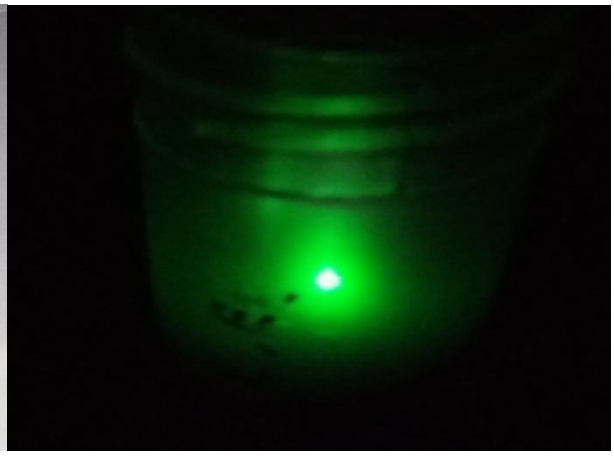

Figure 4.5 (b): Emission in green color upon excitation at 980 nm

In summary, synthesis and characterizations of rare earth (Yb, Er) doped Bi_2O_3 phosphors have been done successfully. It was confirmed from the XRD patterns that Monoclinic phase with high crystallinity is observed. It is also observed that by increasing the concentration of Er, there is decrease in the crystallite size of the Bi2O3:Yb, Er phosphors. FTIR studies show structural properties and presence of different groups and bonds in the synthesized material. SEM images show the surface topography of the synthesized materials. It has been clear from the SEM images that a rod like crystals is formed. EDAX analysis confirms the presence of dopants (Yb, Er) into the host material (Bi_2O_3). NIR fluorescence study confirmed that synthesized rare earth (Yb, Er) doped Bi_2O_3 phosphors are to be liked Up-conversion phosphor.

Acknowledgements

This work is supported by UGC – RFSMS fellowship. The authors would like to thank UGC, NEW DELHI for this great help.

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