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Synthesis and Photoluminescence Properties of $Ba_2B_2O_5:Pr_{0.02}^{3+},Gd_{0.1}^{3+}$

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Abstract

The powder sample of $Ba_2B_2O_5:Pr_{0.02}^{3+},Gd_{0.1}^{3+}$ have been prepared by a method which is slight variation of combustion synthesis. The synthesized materials were characterized by the powder X-ray diffraction and Scanning Electron Microscope (SEM). The photoluminescence properties of prepared phosphors were investigated using a spectroflurometer at room temperature. The synthesized phosphor shows the emission in the UVB region of electromagnetic spectrum, which is a narrow band around 313 nm corresponding to $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition, upon excitation with 254 nm. The energy absorbed by Pr^{3+} was found to be effectively transferred to Gd^{3+} ions in prepared phosphor. The Stoke shift was calculated to be 8370 cm^{-1}.

Keywords: *Narrowband UVB, Phototherapy.*
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INTRODUCTION

According to biological and physical characteristics, ultraviolet radiations are separated such as UV-C: the rays that do not pass through the earth's atmosphere (200-290 nm) UV-B: the rays responsible for nearly all biological effects following sun light exposure including tanning, burning and skin cancer, (290-320 nm) and UV-A: those rays closest to the visible spectrum that pass through glass and are the least harmful to the skin (320-400nm) [1].

Ultraviolet radiation (UVR) is well established for treating the more than 40 skin diseases such as psoriasis [2], or vitiligo [3], which could be treated by UV-B radiation, and lichen sclerosus [4], morphea [5] scleroderma [6], cutaneous T-cell lymphoma, lupus erythematosus [7,8].

Ultraviolet B (UVB) has become the phototherapy treatment of choice for psoriasis, vitiligo, atopic dermatitis (eczema) and other photo-responsive skin disorders. UVB can be divided as narrow-band UVB and broadband UVB. Broadband UVB radiation has been used for the treatment of Psoriasis for decades [9]. Various investigations imply that the Narrowband ultraviolet-B (NB-UVB, 311-313 nm) is the most favourable range phototherapy than the Broad band ultraviolet-B radiation.

Host lattices which are easily synthesizable and structurally viable for doping at multiple cationic sites present in the lattice are of recent interest. The borate atom has two types of hybridized orbitals, the planar sp^2 and the three dimensional sp^3, to coordinate three or four oxygen atoms to form various B_xO_y complex anionic groups. Therefore many types of borate crystals have been found to be constructed based on these complex anionic groups [10]. Therefore, inorganic borates have long been a focus of research. They are excellent host materials because of their variety of structure type, large electronic band gap, transparency to a wide range of wavelengths, high optical damage threshold and high optical quality [11-13]. The phosphors $LaB_3O_6:Gd^{3+}$, Bi^{3+} and $CeMgB_5O_{10}:Gd^{3+}$ are used for narrow UVB phototherapy lamps. In our previous work, we have reported some UV emitting phosphor materials such as $Na_2La_2B_2O_7$ [14], $Sr_2Mg(BO_3)_2:Pb^{2+}$, Gd^{3+} [15], $KCa_4(BO_3)_3:Pb^{2+}$ [16], YBO_3 [17] and $Sr_2Mg(BO_3)_2:Pr^{3+}$, Gd^{3+} [18].

In the present work, the phosphor $Ba_2B_2O_5:Pr_{0.02}^{3+}\_Gd_{0.1}^{3+}$ was prepared using solution combustion synthesis technique. The concentration of Pr^{3+} and Gd^{3+} were decided by referring our previous work. The phase purity of synthesized materials was determined using the powder X-ray Diffractometer. Surface morphology was studied using Scanning Electron Microscope. The photoluminescence properties of the synthesized material were studied using a spectrofluorometer at room temperature.

2. EXPERIMENTAL

2.1 Synthesis of material

Borate phosphor $Ba_2B_2O_5$: $Pr_{0.02}^{3+}\_Gd_{0.1}^{3+}$ was prepared by a method described in our earlier work [19], which is a variation of the combustion

synthesis. Heat generated in the exothermic reaction between ammonium nitrate and urea was used to carry out the synthesis. Table 1gives the details of the ingredients used in synthesis of phosphors. Following the combustion, the resulting fine powders were annealed for 4 h. at temperature 800ºC and then rapidly cooled to room temperature.

Table 1: Molar ratios of the ingredients used for the preparation of the phosphor.

Chemicals grade	SD Fine Chemicals (99.9 % pure)	SD Fine Chemicals (99.9 % pure)	SD Fine Chemicals (99.9 % pure)	SD Fine Chemicals (99.9 % pure)	SD Fine Chemicals (99.9 % pure)	SD Fine Chemicals (99.9 % pure)
Chemical name	$Ba(NO_3)_3$	H_3BO_3	$Pr(NO_3)_3$	$Gd(NO_3)_3$	$CO(NH_2)_2$	NH_4NO_3
Mol	1.88	2	0.02	0.1	5	5
Reaction	$1.88Ba(NO_3)_3 + Bi(NO_3)_3 + Gd(NO_3)_3 + 2H_3BO_3 \rightarrow BaB_2O_5:Pr_{0.02}^{3+}\_Gd_{0.1}^{3+} + CO_2 + NO_3 + CO + NO_x$					

2.2. Characterization of samples

The phase purities of $Ba_2B_2O_5:Pr_{0.02}^{3+}\_Gd_{0.1}^{3+}$ sample was studied using Rigaku miniflex II X-ray Diffractometer with scan speed of 6.000_/min and Cu Ka (λ = 1.5406 Å) radiation in the range 10-90º. PL and PL excitation (PLE) spectra were measured on (Hitachi F-7000) fluorescence spectrophotometer at room temperature. The parameters such as spectral resolution, width of the monochromatic slits (1.0 nm), photomultiplier tube (PMT) detector voltage and scan speed were kept constant throughout the analysis of samples.

3. RESULT AND DISCUSSION

3.1 Structural properties

The crystalline phase of the phosphor $Ba_2B_2O_5:Pr_{0.02}^{3+},Gd_{0.1}^{3+}$ was confirmed by XRD pattern, as shown in Fig. 1. The XRD pattern matched well with the standard data from ICDD file (00-024-0087). $Ba_2B_2O_5$ has a monoclinic crystal structure with a space group of P2/m and lattice parameters values, a=11.014 Å, b=12.684 Å and c=16.586 Å.

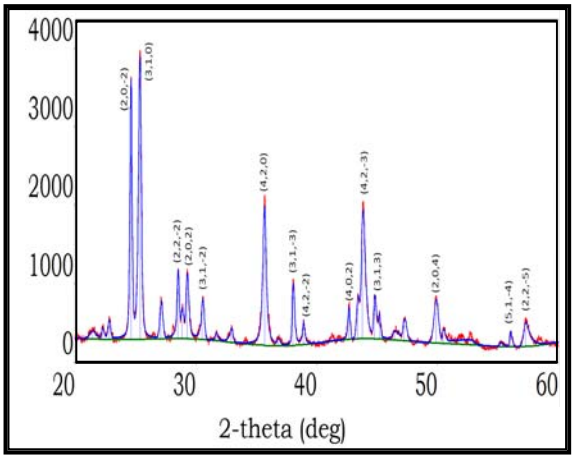

Fig 1. XRD pattern of $Ba_2B_2O_5:Pr_{0.02}^{3+}\_Gd_{0.1}^{3+}$

3.2 Morphological Study

Fig. 2 shows the FE-SEM images of $Ba_2B_2O_5:Pr_{0.02}^{3+}\_Gd_{0.1}^{3+}$ powder prepared at 900 ºC. It was observed that the microstructure of the phosphor consisted of irregular grains. The phosphor show slight agglomeration because of high temperature heating. The average size of particles was observed to be 1- 5 µm.

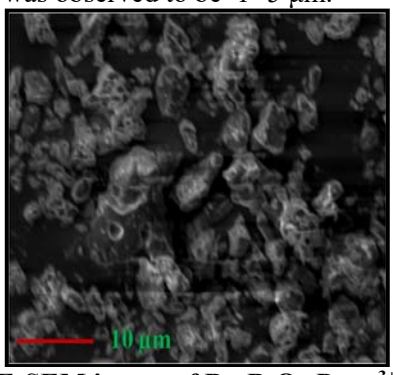

Fig 2. FE-SEM image of $Ba_2B_2O_5:Pr_{0.02}^{3+}\_Gd_{0.1}^{3+}$ phosphor

3.3 Photoluminescence

Fig. 3 represents the photoluminescence emission and excitation spectra of $Ba_2B_2O_5:Pr_{0.02}^{3+},Gd_{0.1}^{3+}$. The emission is in form of a narrow band round 311 nm corresponding to $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition upon excitation with 254 nm. The broad excitation spectrum, shows very good overlap with the Hg 253.7 nm line, has a maximum located at 248 nm, is due to overlap of - $4f^15d^1$ intra-configurational transition of Pr^{3+} and $^8S_{7/2} \rightarrow {}^6D_J$ transition of Gd^{3+} and a weak intense band at about 275 nm corresponding to $^8S_{7/2} \rightarrow {}^4I_J$ of Gd^{3+}. From this, it can be concluded that most of

the excitation energy is absorbed by Pr^{3+} ions. The emission is in form of a narrow band at 313 nm which corresponds to $^6P_J \rightarrow {}^8S_{7/2}$ transition of Gd^{3+} and no traces of Pr^{3+} emission was observed in the emission spectra; this suggests that the energy is effectively transferred from $Pr^{3+} \rightarrow Gd^{3+}$ ions in $Ba_2B_2O_5:Pr_{0.02}^{3+}\_Gd_{0.1}^{3+}$ phosphor.

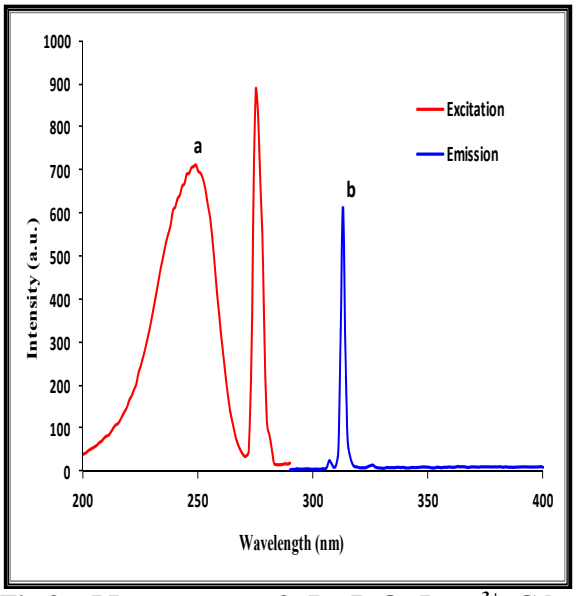

Fig.3. PL spectra of $Ba_2B_2O_5:Pr_{0.02}^{3+}\_Gd_{0.1}^{3+}$ (a)Excitation spectra monitored at 311 nm emission, & (b)Emission spectra monitored at 254 nm excitation.

4. CONCLUSION

The inorganic narrow UVB emitting $Ba_2B_2O_5:Pr_{0.02}^{3+}\_Gd_{0.1}^{3+}$ phosphor was prepared by solution combustion Synthesis method. The XRD pattern of prepared sample was in agreement with the respective ICDD file. SEM image showed irregular grain size with slight agglomeration phenomena. The photoluminescence spectra indicated that the phosphor $Ba_2B_2O_5:Pr_{0.02}^{3+}\_Gd_{0.1}^{3+}$ show narrow UVB emission at 311 nm, upon excitation with 254 nm. The phosphor might be a potential candidate for phototherapy lamps.

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