



SYNTHESIS AND PHOTOLUMINESCENCE STUDY OF UVB EMITTING PHOSPHOR (LaY)BaB₉O₁₆:Bi³⁺,Gd³⁺

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ABSTRACT

(LaY)BaB₉O₁₆:Bi³⁺,Gd³⁺ phosphor is synthesized by the solution combustion synthesis method. The phase analysis of synthesized material is determined using the powder XRD. Photoluminescence properties and concentration quenching were systematically investigated. The phosphor shows the characteristic narrow band UVB emission of Gd³⁺ ions (⁶P_J → ⁸S_{7/2}). The maximum intensity of luminescence in synthesized materials was investigated. The energy transfer mechanism was studied using Bi³⁺ as sensitizers and it is observed that Bi³⁺ effectively transfer its energy to Gd³⁺. The stoke shifts of phosphor was calculated to 6410 cm⁻¹ respectively.

KEYWORDS: Inorganic Borate, Combustion synthesis, Luminescence, NB-UVB emitter.

INTRODUCTION

Rare earth activated borate host phosphors for UV emitting applications are of interest of many researchers since few decades. SrB₄O₇:Eu²⁺ [1], Ba₂B₅O₉Cl:Eu²⁺ [2] are some examples of commercial phosphor used for phototherapy application such as psoriasis treatment and dermatology.

UV radiation has three wavelength zones: UV-A (320-400 nm), UV-B (280-320 nm), and UV-C (200-280 nm), and it is this last region the short wave UV-C, which has germicidal properties for disinfection. A low pressure mercury lamp resembling a fluorescent lamp produces a UV light in the range of 254 nm. Since most micro-organisms are affected by radiation around 260 nm, UV radiation is in the appropriate range for germicidal activity. There are UV lamps that produce radiation in the range

of 185 nm that are effective on microorganisms and will also reduce the total organic carbon (TOC) content of the water.[3]

UV-C light, which continues to be a reliable means of disinfection, involves exposing contaminated water to radiation from UV light. The treatment works because UV-C light penetrates an organism's cell walls and disrupts the cell's genetic material, making reproduction impossible. UV treatment breaks down or removes some organic contaminants. UV achieves 1-log reduction of Giardia lamblia at an intensity of 80-120 mWs/cm², and 4-log reduction of viruses at an intensity of 90-140 mWs/cm². Only recently has the scientific community begun to accept UV as a highly effective tool for Cryptosporidium control. Recently the scientific community has begun to accept UV as a highly effective tool for Cryptosporidium control.[4]

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 sp² and the three dimensional sp³, 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.[5] Therefore, inorganic borates have long been a focus of research. Inorganic borates 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.[6-9]

In our previous work we discussed the energy transfer scheme from Pr³⁺ to Gd³⁺ in YBO₃ [10]. In present paper we discussed the

time saving solution combustion synthesis of a UV-B emitting phosphors $(La_xY_y)BaB_9O_{16}:Bi_{0.02}^{3+}_Gd_{0.1}^{3+}$, and its photoluminescence properties at room temperature.

MATERIALS AND METHODS

$(La_xY_y)BaB_9O_{16}:Bi_{0.02}^{3+}_Gd_{0.1}^{3+}$ phosphors were prepared by a novel method which is a variation of the combustion synthesis, discussed in detail in our previous work [11-13]. In last year our work on NB-UVB emitting phosphor is provided. [14, 15] The method based on exothermic reaction in which ammonium nitrate used as oxidizer and urea is used as fuel. The stoichiometric amounts of high purity starting materials $La(NO_3)_3$, $Y(NO_3)_3$, $Ba(NO_3)_2$, $Gd(NO_3)_3$ (A.R.), $Bi(NO_3)_3$ (A.R.), H_3BO_3 (A.R.), $CO(NH_2)_2$ (A.R.), NH_4NO_3 (A.R.) have been used for preparation of phosphors. Details of molar ratio of ingredients used for phosphors

Table 1: Molar ratio of ingredients used for phosphor synthesis:

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)	SD Fine Chemicals (99.9 % pure)	SD Fine Chemicals (99.9 % pure)
Chemical name	$La(NO_3)_3$	$Y(NO_3)_3$	$Ba(NO_3)_2$	H_3BO_3	$Bi(NO_3)_3$	$Gd(NO_3)_3$	$CO(NH_2)_2$	NH_4NO_3
Mol	0.78 0.68 0.58	0.1 0.2 0.3	1	9	0.02	0.1	5	5
Chemical Reaction	$La(NO_3)_3 + Y(NO_3)_3 + Bi(NO_3)_3 + Gd(NO_3)_3 + Ba(NO_3)_2 + H_3BO_3 \rightarrow (LaY)BaB_9O_{16}:Bi_{0.02}^{3+}_Gd_{0.1}^{3+} + CO_2 + NO_3 + CO + NO_x$							

RESULTS AND DISCUSSION

X-ray Diffraction Pattern

X-ray diffraction study for confirmation of the structure of the phosphor material were studied using instrument Rikagu Miniflex II X-ray Diffractometer with CuK α radiation (1.5406

Å), with a scan speed of 2° min^{-1} . The compound $(Y_{1-x}La_x)BaB_9O_{16}$ crystallizes in a Hexagonal structure with lattice parameters $a=b=7.878 \text{ \AA}$, & $c=15.632 \text{ \AA}$. The XRD pattern was found to be in good agreement with the ICDD file no.: **00-041-0620**.

The structural analysis of the synthesized materials were examined using an X-ray Diffractometer (XRD: Rigaku Maniflex II, with CuK α irradiation ($\lambda=1.5406 \text{ \AA}$) with a scan speed of 2° min^{-1} . The photoluminescence excitation and emission spectra were measured at room temperature using Hitachi F-7000 Spectrofluorometer in the range 200-500 nm.

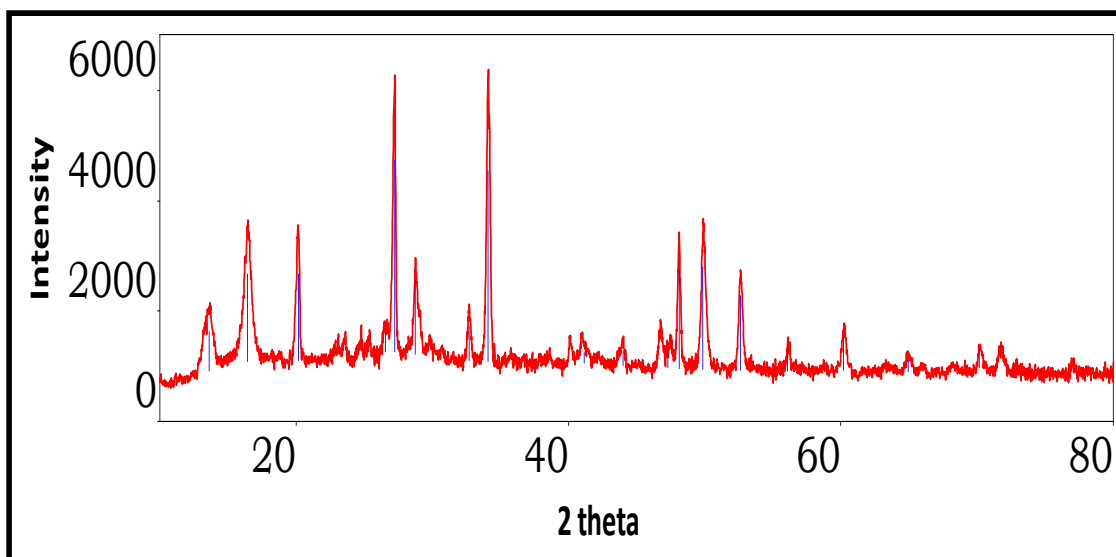


Fig.1: XRD pattern of prepared phosphor material $(\text{LaY})\text{Ba}_9\text{O}_{16}:\text{Bi}_{0.02}^{3+} \text{ _Gd}_{0.1}^{3+}$.

SEM images

Fig.4.20 shows the SEM images of $(\text{LaY})\text{Ba}_9\text{O}_{16}:\text{Bi}_{0.02}^{3+} \text{ _Gd}_{0.1}^{3+}$ powder prepared at 800°C . It was observed that the microstructure of the phosphor consisted of irregular grains with

agglomerate phenomena. The average size of synthesized phosphor particles was found to be about $1\text{--}5\ \mu\text{m}$. The results show that phosphors have a good crystallinity and a relatively low sinter temperature.

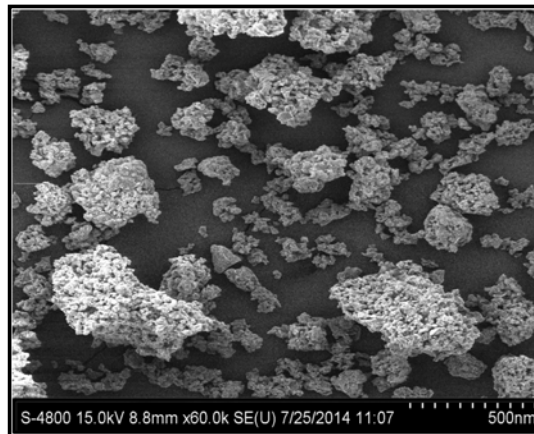
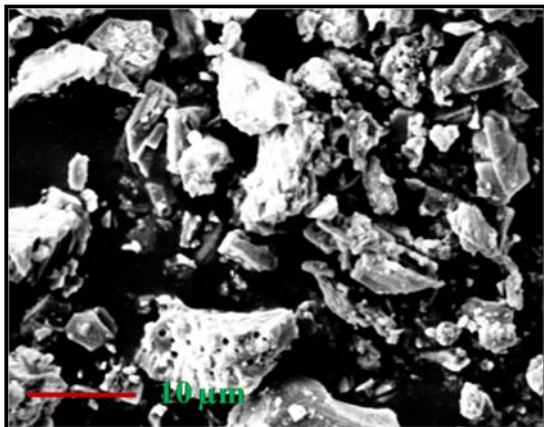


Fig.2: SEM image of $(\text{LaY})\text{Ba}_9\text{O}_{16}:\text{Bi}_{0.02}^{3+} \text{ _Gd}_{0.1}^{3+}$.

Photoluminescence Analysis

To study the effect of substitution of Y for La, different concentration of Y and La were used and their photoluminescence were studied. But no remarkable changes were observed in the emission and excitation spectra. Therefore, only the optimum one emission and excitation spectra for concentration of $\text{La}=0.78$ and $\text{Y}=0.1$ is shown in the Fig.3. In our previous work on $\text{YBa}_9\text{O}_{16}:\text{Bi}^{3+},\text{Gd}^{3+}$ the optimum intensity of emission was observed for the concentration at $0.02\ \text{mol}\%$ and $0.03\ \text{mol}\%$ of Bi^{3+} and Gd^{3+} respectively. [16] Excitation and emission spectra were studied using instrument Hitachi 7000 spectrophotometer, slit width $1\ \text{nm}$ and

PMT voltage $700\ \text{V}$. Figure 4 represents the PL spectra of $(\text{LaY})\text{Ba}_9\text{O}_{16}:\text{Bi}_{0.02}^{3+} \text{ _Gd}_{0.1}^{3+}$. The emission is in form of a narrow band around $312\ \text{nm}$ corresponding to ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$ transition upon excitation with $254\ \text{nm}$. The broad excitation spectrum has a maximum located around $260\ \text{nm}$ corresponds to ${}^1\text{S}_0 \rightarrow {}^3\text{P}_1$ transition of Bi^{3+} ions. As the intensity of phosphor materials is beyond the limit of instrument used, the cut in the upper part of emission and excitation spectra is observed. The excitation spectra show very good overlap with the Hg $253.7\ \text{nm}$ line. The efficient energy transfer from Bi^{3+} to Gd^{3+} is observed. The stoke shift was calculated to be $6410\ \text{cm}^{-1}$.

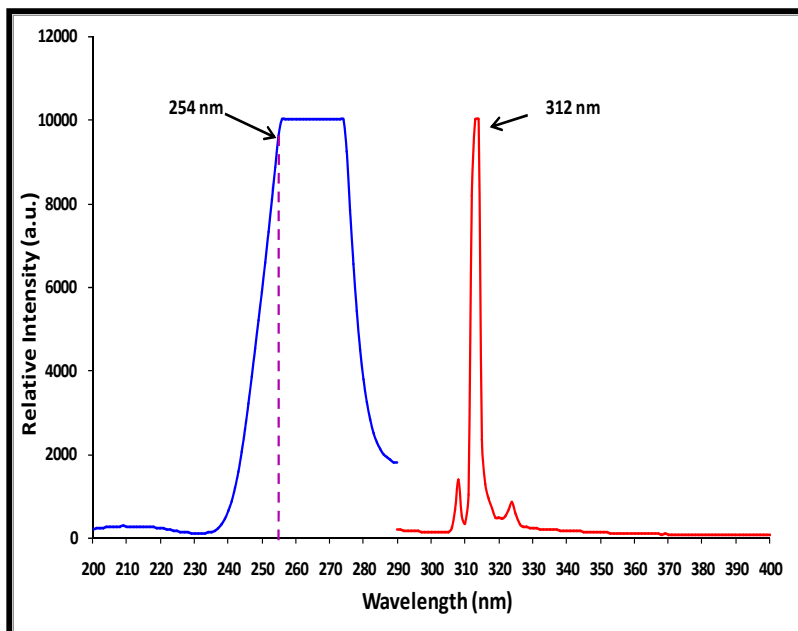


Fig.3: Emission monitored at 254 nm and excitation monitored at 311 nm.

CONCLUSION

$(\text{La}_x\text{Y}_y)\text{BaB}_9\text{O}_{16}:\text{Bi}_{0.02}^{3+}\text{Gd}_{0.1}^{3+}$ phosphors have been successfully synthesized by using time saving solution combustion synthesis technique. The room temperature photoluminescence of synthesized phosphors show emissions at wavelength 312 nm corresponding to ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$ transition upon excitation with 254 nm. This emission wavelength lies in the UV-B region of electromagnetic spectrum. The stoke shift was calculated to be 6410 cm^{-1} . The phosphor could find applications in medical and industries for phototherapy applications.

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