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COMMUNICATION

Effect of Y:B ratio on phase purity and development of thermally stable nano-sized Eu^{3+} -doped YBO_3 red phosphor using sodium borohydride

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Shubham Srivastava, Shantanu K. Behera, Bibhuti B. Nayak*

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This research focuses on effect of Y:B ratio on phase purity and the development of thermally stable 10 mol % Eu^{3+} -doped YBO_3 red phosphor nanomaterials using novel sodium borohydride based solution precursor route. Equimolar concentration of Y and B lead to the development of chemically and thermally stable un-doped and Eu^{3+} -doped YBO_3 up to 1300 °C. An impurity phase, Y_3BO_6 , was observed at a higher temperature of around 1400°C. FESEM micrographs indicate that the particles of Eu^{3+} -doped YBO_3 are agglomerated with peanut-like morphology having average size ~50 nm at 800 °C, whereas, the average agglomerated size was in between ~200 nm to 1.5 μm , at 1200 °C. The particles of Eu^{3+} -doped YBO_3 are nearly spherical having size ~8-10 nm at 800 °C and the size increases in the range of ~30-100 nm at 1200 °C, as observed from TEM micrographs. Additionally, the borohydride synthesized Eu^{3+} -doped YBO_3 phosphor calcined at 800 °C showed comparatively better colour purity (denoted as R/O ratio i.e. integral ratio of red to orange emission = 1.25) than high temperature (1200 °C) calcined sample (R/O ratio = 0.97). Both the calcined powders indicated nearly reddish-orange colour based on calculated Commission Internationale de l'Eclairage (CIE) coordinates. The synthesis strategy followed in the current research work emphasizes the feasibility of synthesizing thermally stable Eu^{3+} -doped YBO_3 red phosphor material by borohydride route, which may be suitable for lighting applications.

Rare earth, such as europium (Eu^{3+}) ion, doped yttrium borate (YBO_3) phosphor material has gathered a lot of attention for use in display applications due to its high chemical and thermal stability and almost complete transparency in ultra-violet (UV) region in conjunction with excellent optical damage threshold^{1,2}. During the manufacturing of phosphors, several vital aspects must be given due consideration; namely morphology and particle size, composition and stoichiometry, stability, together with the nature and shape of the particle surface^{3,4}. Exploring and

understanding these nanophosphors is of pivotal importance for developing smart devices of technological relevance for advanced phosphor and photonic applications. Different synthesis strategies, including conventional solid state, sol-gel, spray pyrolysis, co-precipitation, hydrothermal and solvothermal have been optimized to develop Eu^{3+} -doped YBO_3 phosphor materials⁵⁻¹². The main challenges concerning the formation of phase pure Eu^{3+} -doped YBO_3 lie in the development of synthesis strategies, optimizing synthesis parameters and amount of boric acid (H_3BO_3). Almost all of these strategies employ H_3BO_3 in general, for the development of this phosphor material. Evidences suggest the use of excess amount of H_3BO_3 to develop phase pure borate phosphors^{13,14}. Moreover, Eu^{3+} -doped YBO_3 phosphors prepared by most of these methods are not phase pure up to a higher temperature above 1000 °C^{11,15}. Higher temperatures lead to the formation of an impurity phase Y_3BO_6 that has been reported to cause a hampering effect on the photoluminescence efficiency¹⁵. Further, the Y: B ratio is a critical parameter for the determination of phase purity of YBO_3 phosphor materials. Many researchers have investigated the effect of Y: B ratio on the formation of YBO_3 phosphors using H_3BO_3 as a boron source^{16,17}. Endeavours have been made to improve colour purity and luminescent efficiency based on different optimized synthesis strategies^{18,19}. Fewer investigations have been pursued with materials other than H_3BO_3 as a boron source, for synthesizing YBO_3 phosphors with comparably or better photoluminescence characteristics. This introduces the necessity of a synthesis procedure that would produce phase pure Eu^{3+} -doped YBO_3 red phosphor materials with higher temperature stability. In this quest, an innovative strategy based on borohydride synthesis route for development of Eu^{3+} -doped YBO_3 materials is disclosed in this paper. Our research group has been a pioneer in preparing different varieties of nano-sized materials including zirconium oxide, metal, metal oxide and metal-ceramic composites using sodium borohydride

Department of Ceramic Engineering, National Institute of Technology, Rourkela-769008, India

*Corresponding address: bbnayak@nitrkl.ac.in, bibhutib@gmail.com (Bibhuti B. Nayak), Phone: 0661-246 2209 Fax: +91-661-2472999

(NaBH_4) as a precipitating agent²⁰⁻²⁴. Efforts are being made to prepare smaller crystallites of $\text{YBO}_3:\text{Eu}^{3+}$ phosphor using sodium borohydride as a boron source and a precipitating agent in order to achieve better photoluminescence characteristics. The goal of this paper is to establish the borohydride synthesis strategy by optimizing Y:B ratio for developing phase pure Eu^{3+} -doped YBO_3 phosphor material with excellent thermal and chemical stability along with better photoluminescence characteristics.

Analytical grade of yttrium oxide (Y_2O_3), europium oxide (Eu_2O_3) and sodium borohydride (NaBH_4) in powder form were used as the starting raw materials. In order to examine the phase purity of YBO_3 , the compositional variation of un-doped YBO_3 was evaluated based on the Y:B molar ratio such as 1:2, 1:1 and 2:1. To prepare un-doped YBO_3 having Y: B molar ratio 1:1, the following two separate precursor solutions were prepared. For the first precursor, aqueous solution of 0.2 M Y_2O_3 was prepared by dissolving it in hydrochloric acid (HCl). For second precursor, aqueous 0.2 M solution of NaBH_4 was prepared by dissolving solid NaBH_4 in distilled water. In a similar way, separate precursor solutions of Y_2O_3 and NaBH_4 were prepared with a variation in Y:B molar ratio such as 1:2 and 2:1. For preparing un-doped YBO_3 having different molar concentration of Y:B, gelation-precipitation method using borohydride route was followed. In this gelation-precipitation method, the borohydride reaction was conducted at room temperature with drop wise addition of aqueous NaBH_4 to the Y_2O_3 precursor solution, with constant stirring using a magnetic stirrer. During addition of aqueous NaBH_4 , the pH of the precursor solution increases and a low viscous gel was formed at pH \sim 7.2. With further addition of aqueous NaBH_4 , this gel was slowly converted to precipitate at pH \sim 9. The reaction was continued until pH 10, where the precipitate starts to settle down. This precipitate was washed several times with distilled water to remove unwanted products. After washing, the precipitate was dried and calcined at different temperatures. Phase analysis was carried out using X-ray diffractometer (Rigaku Ultima-IV X-Ray Diffractometer with $\text{Cu K}\alpha$ radiation with $\lambda=1.5406 \text{ \AA}$). After analysing the phase purity of YBO_3 in the above condition, 10 mol % Eu^{3+} ions was further doped in to YBO_3 system in the optimized Y: B ratio (i.e. 1:1) for preparing $\text{YBO}_3:\text{Eu}^{3+}$ red phosphor material. During synthesis of Eu^{3+} -doped YBO_3 , 0.2 M aqueous solutions of 90 mol % Y_2O_3 and 10 mol % Eu_2O_3 were prepared by dissolving the appropriate quantity of respective powders in hydrochloric acid (HCl). The same gelation-precipitation method was followed as stated above using 0.2 M concentration of aqueous NaBH_4 . After the reaction, precipitate was washed, dried and calcined at different temperatures. Phase analysis of Eu^{3+} -doped YBO_3 was performed using XRD. The morphology of the prepared samples was studied by Field Emission Scanning Electron Microscopy (Nova Nano SEM/FEI 450) and TEM (JEM-2100, JEOL). The photoluminescence spectra of prepared solid $\text{YBO}_3:\text{Eu}^{3+}$ powder sample were measured at an excitation wavelength of 230 nm with the help of fluorescence spectrometer (Horiba Jobin Yvon,

USA/Fluoromax 4P) using slit width of 2.5 nm and source of 150 watt ozone free xenon lamp. The excitation wavelength of 230 nm was chosen based on Figure S1 in ESI. The fluorescence microscopy images were captured with the help of fluorescence microscope (Olympus IX-71 Corporation Tokyo, Japan). The color chromaticity coordinates were obtained according to Commission Internationale de l'Eclairage (CIE) using 1931 2-degree standard observer.

The as-synthesized un-doped YBO_3 prepared by varying molar concentration of Y: B ratio was calcined at 800 °C in order to study the favourable condition for formation of phase pure crystalline YBO_3 . XRD patterns in Figure 1 represent the calcined (800 °C) un-doped YBO_3 samples prepared at three different conditions of Y: B ratio such as 1:2, 1:1 and 2:1.

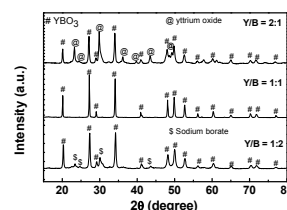


Fig. 1: XRD patterns of calcined (800 °C) pure YBO_3 prepared by varying Y: B ratio.

Among these three samples, the phase pure YBO_3 is formed when the molar concentration of Y:B was kept at 1:1. However, either excess of 'B' or 'Y' in the samples having Y: B ratio of 1:2 or 2:1 indicate the formation of some additional impurity phases along with YBO_3 . The impurity phases are identified with sodium borate (JCPDS file number: 22-1351) and oxygen deficient yttrium oxide (JCPDS file number: 39-1063 and 39-1065) for the samples prepared for Y:B equal to 1:2 and 2:1, respectively. XRD evidence suggests that differences in molar concentration in Y: B ratio between these three samples are a reflection of the fact that Y: B ratio plays a rather important role in the development of phase pure YBO_3 . In turn, it implies that the feasible condition for the development of a phase pure sample using this method is when equimolar concentration of the precursors is used. To better understand the high temperature phase stability, un-doped YBO_3 and 10 mol % Eu^{3+} -doped YBO_3 (equimolar ratio of Y:B) were calcined at different temperatures (800 °C, 1000 °C, 1100 °C, 1200 °C, 1300 °C and 1400 °C) and XRD was performed. Fig. 2 (a) and (b) depicts XRD patterns of un-doped and Eu^{3+} -doped YBO_3 samples heat-treated at different temperatures, respectively.

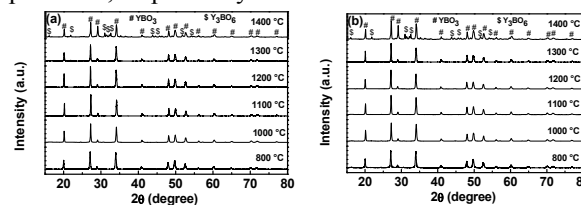


Fig. 2: XRD patterns of un-doped (a) and Eu^{3+} -doped (b) YBO_3 (Y: B ratio 1:1) calcined at different temperatures.

From XRD patterns it was revealed that the borohydride synthesized un-doped and Eu^{3+} -doped YBO_3 is stable up to 1300 °C and the formation of Y_3BO_6 phase is detected at 1400

°C. This value is higher than a few preceding reports which concerned with the formation of Y_3BO_6 phase^{25,26}. The phase Y_3BO_6 has been reported at comparatively lower temperatures of 1000° and 1100° C and is detrimental for the photoluminescence properties of the corresponding phosphor^{11,15}. Generally, the formation of Y_3BO_6 strongly depends on the stoichiometric concentration of the starting material. Also, the boron composition may reduce due to evaporation of boron oxide during calcination process^{25,27}. The evaporation of boron oxide may vary from moderate temperature to higher temperature, depending on the homogeneity of Y: B ratio throughout the sample. In the present study, we speculate that the Y: B ratio is maintained homogeneously throughout the sample, which leads to the delay in phase formation of Y_3BO_6 . With subtle loss of B_2O_3 at higher temperature, the stoichiometric of the studied system becomes slightly Y_2O_3 rich. In other words, the Y/B ratio increases slightly over 1. In such a situation, YBO_3 and Y_3BO_6 are the thermodynamically stable phases, where the amount of Y_3BO_6 formed depends on the extent of B_2O_3 loss. The crystallite size of these heat-treated samples is given in Table S1 based on Scherrer's formula and the values were found to vary from ~35 nm to ~50 nm. The powders calcined at 800 °C exhibited slightly increased lattice parameters. However, powders calcined at 1000 °C and upwards showed no appreciable change in the lattice parameters. The lattice parameter of Eu^{3+} -doped YBO_3 sample is slightly higher than the un-doped YBO_3 sample (Lattice parameter and cell volume of all samples are given in ESI, Table S1). The phase pure $YBO_3:Eu^{3+}$ is stable up to a high temperature to elucidate the chemical stability of prepared sample, which shows that the material is suitable to be availed for harsh conditions in plasma display panels (PDPs). Based on the thermal stability of YBO_3 , it was interesting to study the microstructure and photoluminescence characteristics of 10 mol % Eu^{3+} -doped YBO_3 , heat-treated at lower (800 °C) and higher (1200 °C) temperatures. To study the powder morphology of un-doped and Eu^{3+} -doped YBO_3 , FESEM as well as TEM images were acquired. FESEM and TEM micrographs of calcined un-doped YBO_3 are added and discussed in ESI, Figure S2 and Figure S3, respectively. For calcined Eu^{3+} -doped YBO_3 powders, FESEM micrographs are shown in Figure 3.

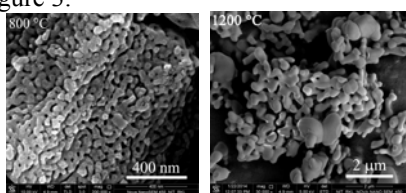


Fig. 3: FESEM micrographs of 10 mol % Eu^{3+} -doped YBO_3

The 800° C calcined Eu^{3+} -doped YBO_3 particles were nearly spherical in nature. The agglomerated particles (size ~ 50 nm) were well-connected and depict peanut-like morphology primarily due to negligible temperature induced coarsening. However, average particle size ranging from ~200 nm to 1.5 μ m was observed for the phosphor calcined at 1200° C. From the elemental mapping and EDS spectra of ESI, Figure S4, it was confirmed that the prepared phosphor

is phase pure having 10% Eu^{3+} , which is well distributed in the YBO_3 matrix. To further confirm the powder morphology, TEM analysis of Eu^{3+} -doped YBO_3 , calcined at 800 °C and 1200 °C was performed and is shown in Fig. 4. In both cases, particles are nearly spherical in nature. The average particle size of $YBO_3:Eu^{3+}$, calcined at 800 °C was found to be around ~8-10 nm, whereas the average particle size was in the range of ~30-100 nm, when calcined at 1200 °C.

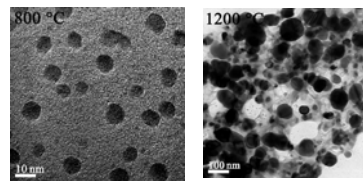


Fig. 4: TEM micrographs of 10 mol % Eu^{3+} -doped YBO_3

The emission characteristics including colour purity and chromaticity coordinates are of imperative significance for a phosphor to be used in display and lighting applications. The emission spectra consist of several sharp lines as indicated in Fig. 5.

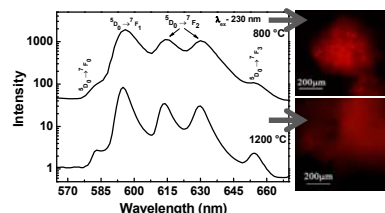


Fig. 5: Emission spectra from 10 mol % Eu^{3+} -doped YBO_3 phosphor calcined at two different temperatures. Fluorescence images in inset indicate that samples are reddish in colour.

All the emission peaks are ascribed to the transition of europium ions from $^5D_0 \rightarrow ^7F_J$ ($J=0, 1, 2, 3$) levels as marked in emission spectra. It can be inferred that the prominent PL emission peaks in the visible range observed for $YBO_3:Eu^{3+}$ are at 595 nm (orange emission due to $^5D_0 \rightarrow ^7F_1$ transition), 614 nm and 630 nm (red emission due to $^5D_0 \rightarrow ^7F_2$ transition). Contribution from $^5D_0 \rightarrow ^7F_1$ corresponds to magnetic dipole transition and $^5D_0 \rightarrow ^7F_2$ corresponds to electric dipole transition²⁸. Colour purity is denoted as R/O ratio [$I(^5D_0 \rightarrow ^7F_2) / I(^5D_0 \rightarrow ^7F_1)$], and is calculated by considering the sum of integral intensity of red emission peaks observed at 614 and 630 nm for contribution of $^5D_0 \rightarrow ^7F_2$ transition. The R/O ratio was found to be 1.25 and 0.97 for 800 °C and 1200 °C calcined Eu^{3+} -doped YBO_3 phosphors, respectively and the higher R/O ratio is mainly due to high surface disorder associated with small particle size^{28,29}. The obtained R/O ratio is higher than the reported R/O ratio of bulk $YBO_3:Eu^{3+}$ phosphor, which varies in the range of 0.36 to 0.5 based on calcination temperature^{19,30}. Furthermore, the R/O ratio is also depending on the wet-chemical synthesis condition as well as excitation wavelength. The R/O ratio was found to be 0.69, 0.74, 0.78 and 0.81 for $Y_{0.9}BO_3:Eu_{0.1}$ phosphor prepared at 260 °C, 240 °C, 220 °C and 200 °C using hydrothermal method at an excitation wavelength of 240 nm¹⁹. Besides, by changing Y: B ratio and using ethanol as a solvent, the R/O ratio of $YBO_3:Eu^{3+}$ varies in the range between 0.99 to 1.29,

when excited at 254 nm and on increasing the excitation wavelength to 363 nm, the R/O ratio changes in between 1.16 to 1.22². Additionally, the R/O ratio was found to be 0.6 for drum like YBO₃:Eu³⁺ microcrystals³¹ and 1.3 for amorphous and spherical YBO₃:Eu³⁺ phosphor³² prepared via hydrothermal method. However, R/O ratio of YBO₃:Eu³⁺ phosphor was found to possess a higher value of 5.1 and 6.692 on using a nominal Eu³⁺ concentration such as 2 mol % and 0.3 mol %, respectively^{10,33}.

Chromaticity coordinates were calculated for further analysis of the phosphor. The x and y chromaticity coordinates were found to be 0.53 and 0.32, respectively for Eu³⁺-doped YBO₃ phosphor calcined at 800 °C in this work. On the other hand, the chromaticity coordinates for higher temperature calcined (1200 °C) Eu³⁺-doped YBO₃ phosphor were found to be nearly same (x = 0.52, and y = 0.32). The corresponding colour based on chromaticity co-ordinates in fact can be classified as reddish-orange. However, from fluorescence microscopy images, as represented in Fig. 4, the colour of the calcined (both 800 °C and 1200 °C) YBO₃:Eu³⁺ powder is nearly reddish. The chromaticity coordinates may also vary from reddish-orange to red, depending on the synthesis condition. In this context, Yadav et. al. reported the chromaticity coordinates (x, y) of Eu³⁺-doped YBO₃ as (0.655, 0.345)¹⁰ by employing co-precipitation method, whereas, Zhang et. al. obtained a value of (0.64, 0.33)² while using hydrothermal method. In addition, co-precipitation method yielded Y_{0.7}BO₃:Eu³⁺_{0.3} phosphor having chromaticity coordinates as (0.6601, 0.3359)³³. Also, the CIE chromaticity coordinates of YBO₃:Eu³⁺ samples prepared via the solvothermal route at 200, 220 and 240 °C were (0.623, 0.376), (0.622, 0.376) and (0.613, 0.386), respectively³⁴. However, Koparkar et al. and Dubey et al. reported the CIE coordinates as (0.539, 0.34)³⁵ and (0.566, 0.393)³⁶, respectively, which are comparable with the results obtained in this work. A decrease in the luminescence intensity was observed with increase in calcination temperature from 800 °C to 1200 °C because of thermal quenching³⁷, the calculated coordinates revealed that the effect of temperature on chromaticity was almost negligible. Inevitably, this discloses that the calcination temperature does not have a radical effect on chromaticity of borohydride derived Eu³⁺-doped YBO₃ phosphor and ensures that the strategy followed in the present work is apt for production of phosphors.

Conclusions

The present work demonstrates the synthesis of inorganic nano-size Eu³⁺-doped YBO₃ red phosphor material, obtained from borohydride based solution-processed strategy. The main deductions drawn from this study are summarized as follows:

- The research establishes sodium borohydride as an alternative boron source required to obtain thermally stable Eu³⁺-doped YBO₃ phosphor materials up to 1300 °C using equal molar concentration of 'Y' and 'B'. Impurity phase Y₃BO₆ is formed at around 1400 °C.
- FESEM micrographs confirmed that the average agglomerated particle size with peanut-like morphology was 50 nm at 800 °C and ~200 nm – 1.5 µm at 1200 °C.

Though, the particles are nearly spherical in shape at both 800 °C and 1200 °C. The average particle size ~ 8-10 nm at 800 °C and ~30- 100 nm at 1200 °C.

- The calcined (800 °C) YBO₃:Eu³⁺ phosphor has comparatively better colour purity (R/O ratio) as that of the phosphor calcined at 1200 °C due to high surface disorder associated with small particle size.
- There are almost no changes in CIE coordinates for both the calcined samples. However, the colour of both samples is nearly reddish-orange based on CIE coordinates and nearly red in colour based on fluorescence image.
- The results and evidences suggest that the borohydride synthesized nano-size YBO₃:Eu³⁺ red phosphor ensures decent spectroscopic properties and optimal chemical stability at moderate as well as high temperatures.

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