Combustion synthesis of Ba$_3$Y$_{1-x}$Sm$^{3+}_{x}$(BO$_3$)$_3$ as red-light emitting phosphors for indoor plant cultivation applications

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Abstract. In this paper, a series of Sm activated Ba$_3$Y(BO$_3$)$_3$ phosphors are synthesized by high-temperature solution combustion method. The concentration of Sm ions is changed from 1 to 5 mol% in the host lattice of BYB crystal. The crystal structure, phase of formation, particle size, elemental analysis, photoluminescence study of synthesized phosphors are done using X-ray diffraction, FE-SEM, Fourier transform infrared spectroscopy (FTIR) and photoluminescent (PL) techniques. The excitation spectra consisted of strong bands in the NUV and blue region. The phosphors on excitation at 449 nm exhibited a strong emission peak in the region 630-660 nm, which corresponds to the absorption spectra of PR phytochrome. The obtained photometric results show that these can be used for the design of light-emitting diodes for indoor plant applications, houseplants gardening and in horticultural fixtures.

Keywords: Red phosphor; samarium; BYB crystal; Indoor plants; phytochrome.

1. Introduction

In the recent scenario, innovations of “horticulture” has been increasing tremendously due to its advantages over the conventional approaches used for the growth of plants under sunlight. Undoubtedly, “natural and artificial” light plays a pivotal role in the development of plants via different plant mechanisms [1–4]. In plants chlorophyll A, chlorophyll B absorbed the light in UV-blue region in the range 420-500 nm and phytochrome (P$_R$), phytochrome (P$_{FR}$) absorbed the light in the “red and far-red” region from 640 to 750 nm [5–7]. The red color plays a vital role in plant growth. Therefore much emphasis has been paid on the development of red phosphors for indoor plant lighting devices. Up to now, many Mn$^{4+}$ and Eu$^{3+}$ doped phosphors have been reported as red light-emitting phosphors for room and greenhouse plant requirement [8–11]. This is due to the reason the emission spectral line of these phosphors match well the absorption lines of Phytochrome P$_R$. In a recent study by Rajendran and Vaidyanathan [12], authors reported for the first time Sm$^{3+}$ activated NaSrY(MoO$_4$)$_3$ phosphors for the fabrication of LEDs for plant growth. In the present report, Sm$^{3+}$ activated Ba$_3$Y(BO$_3$)$_3$ phosphor...
for indoor plant applications synthesized via combustion route. It is found that under blue excitation at 449 nm, the phosphors exhibit wide emission spectra from 630 nm to 660 nm, which matches well with the absorption spectra of P2. Thus, this phosphor can be used for the development of Light emitting diodes for in-house plant applications, for sun-shed plant growth, and indoor gardening.

$\text{Ba}_3\text{Y(BO}_3)_3$ belongs to the $\text{M}_3\text{Ln(BO}_3)_3$ family [13]. The BYB crystal exists in two structures i.e., low-temperature $\alpha$-$\text{Ba}_3\text{Y(BO}_3)_3$ with space group $\text{P6}_3\text{cm}$ and high-temperature $\beta$-$\text{Ba}_3\text{Y(BO}_3)_3$ with space group $\text{R3}$. The photoluminescence properties under doping are different for both phases. The structure of low-temperature phase $\alpha$-$\text{Ba}_3\text{Y(BO}_3)_3$ is consist of boron atoms with three fold coordination number and Ba sites with 9 coordination number are separated by parallel planes of anion group. The crystal structure is comprised of isolated $\text{BO}_3^-$ and $\text{Ba}$ ions having sixfold coordinates, yttrium ions having sixfold coordinates, barium atoms having nine and six coordinates [14]. Maggagay et al. synthesized the $\text{Ba}_3\text{Y(BO}_3)_3$: Eu$^{3+}$, Bi$^{3+}$ phosphor via solid-state reaction and studied it as a phosphor for w-LEDs using N-UV LED chips [15]. Wu et al. described $\text{Ba}_3\text{Y(BO}_3)_3$: Sm$^{3+}$ as potential orange-red phosphors for white LEDs [16]. Yu et al. investigated luminescent and energy transfer in $\alpha$-$\text{Ba}_3\text{Y(BO}_3)_3$:Ce$^{3+}$, Tb$^{3+}$ [17]. In the present work, the synthesis of $\text{Ba}_3\text{Y(BO}_3)_3$:Eu$^{3+}$ activated $\text{Ba}_3\text{Y(BO}_3)_3$ phosphors by solution combustion method is a new approach. The luminescent properties of Sm$^{3+}$ activated $\text{Ba}_3\text{Y(BO}_3)_3$ prepared by solution combustion method is not described yet. All the results are studied in detail.

2. Experimental

2.1 Materials & synthesis

Sm activated $\text{Ba}_3\text{Y(BO}_3)_3$ phosphors were synthesized using modified solution combustion route. SCS involves highly exothermic redox chemical reaction. It is chain of flaming, smoldering and explosive reaction. The starting precursors $\text{Ba(NO}_3)_2$, $\text{Y(NO}_3)_3$, $\text{H}_3\text{BO}_3$, and $\text{Sm(NO}_3)_2$, $\text{H}_2\text{O}$ of analytical grade were taken according to stoichiometric ratio $\text{Ba}_3\text{Y}_x\text{Sm}_7\text{(BO}_3)_3$ ($x = 0.005$, 0.01, 0.02, 0.03, 0.04, 0.05, 0.01). As a source of Boron, Boric Acid is used. The compound is neutral. So neither extra oxidizer nor fuel is necessary for solution combustion synthesis. In 10 to 20ml double distilled water all precursors were dissolved. In this solution, fixed amount urea as a fuel was added calculated using propellant chemistry [18]. The solution was stirred on hot plate magnetic stirrer maintained at a temperature of 90°C for 50 min. The viscous solution formed was transferred to Platinum crucible and kept into a 700°C preheated muffle furnace. Within few minutes, the water evaporated and combustion reaction took place with the liberation of gases. The resulting foamy powder was grounded gently into a fine powder and subjected to further heat treatment at 950°C for 5 hours in a muffle furnace in reducing environment. Reducing environment was developed using activated charcoal. After heating the obtained phosphors were grounded into fine powder and used for further characterizations.

2.2 Characterizations

XRD of synthesized phosphor were recorded by Rigaku Miniflex II X-ray diffractometer using the Cu-K$_\alpha$ radiations ($\lambda = 1.54060\ \text{Å}$) and scanning in the 20 range from 10-80°. The obtained patterns were compared with the available ICSD file. The Fourier transform infrared spectra (FTIR) were recorded in the 300-4000 cm$^{-1}$ range using FTIR spectrophotometer Model RZX (Perkin Elmer). The surface morphology and elements studies were done by scanning electron microscopy [Model JSM6100 (JEOL)]. The emission and excitation spectra were recorded using F-7000 FL spectrophotometer with a scan speed 240 nm/min. The width of the slit for excitation-emission spectra was set 1 nm. All the characterizations were done at room temperature.

3. Results and Discussion

X-ray diffractograms were recorded to determine the phase and crystal structure of the synthesized phosphors. $\text{Ba}_3\text{Y(BO}_3)_3$ host lattice possesses hexagonal crystal structure with the space group $\text{P6}_3\text{cm}$ (No.185). All $\text{BO}_3^-$ ions are coordinated with three $\text{O}^2-$ ions forming the $\text{BO}_3^-$ triangles. Y sites with six co-ordination number and Ba sites with 9 co-ordination number are separated by parallel planes of $\text{BO}_3^-$ anion group. The crystal structure is comprised of isolated $\text{BO}_3^-$ triangles, $\text{YO}_6$ octahedral and
BaO₄ polyhedral. Figure 1 represents the XRD patterns of Ba₃Y₀.₉₇(BO₃)₃:₀.₀₃Sm³⁺ phosphors. The XRD patterns are well-matched with the standard inorganic crystal structure (ICSD) file (reference no. 99537) of the Ba₃Y(BO₃)₃ structure.

![Figure 1. XRD & ICSD file of Ba₃Y₀.₉₇(BO₃)₃:₀.₀₃Sm³⁺ phosphor](image)

Figure 2 represents the FTIR spectra of the of Ba₃Y₀.₉₇(BO₃)₃:₀.₀₃Sm³⁺ sample in the region 300-4000 cm⁻¹. The strong bands above 1100 cm⁻¹ are due to the B-O stretching mode of the triangular [BO₃]⁻ groups [19]. The bands in the range 700-800 cm⁻¹ correspond to the B-O out of plane bending vibration, which confirms the presence of the [BO₃]⁻ groups. Due to the complete combustion of nitrate and organic matter peaks in 1500–2000 cm⁻¹ were absent. The presence of peak at 523 cm⁻¹ relates to the Y-O vibrational motion[20].

![Figure 2. FTIR of Ba₃Y₀.₉₇(BO₃)₃:₀.₀₃Sm³⁺](image)
The “SEM micrographs” of Ba$_3$Y$_{0.97}$(BO$_3$)$_2$:0.03Sm$^{3+}$ phosphors at various magnifications are displayed in figure 3 (a-b). From the microstructures, it seems to be that the particles consist of non-uniform grains with agglomeration. The cause of the agglomeration is due to the high-temperature treatment [21]. The “Average particle size” is in the sub-micrometer range due to the “agglomeration of the particles”. Fig. 4 represents the EDX spectra of Ba$_3$Y$_{0.97}$(BO$_3$)$_2$:0.03Sm$^{3+}$ phosphors. The spectra consist of Ba, Y, B, O, and Sm elements. No other elements than these are found, which represent that organic residues are completely removed. These results are “Consistent with the FTIR and XRD” results.

**Figure 3.** (a-b) SEM micrographs of Ba$_3$Y$_{0.97}$(BO$_3$)$_2$:0.03Sm$^{3+}$ phosphor at different magnifications

**Figure 4.** EDX spectra of Ba$_3$Y$_{0.97}$(BO$_3$)$_2$:0.03Sm$^{3+}$ phosphor

Figure 5 represents the PL excitation spectra (PLE) of Ba$_3$Y$_{0.03}$(BO$_3$)$_2$: 0.03Sm$^{3+}$ recorded in the region 300-550 nm at 644 nm emission wavelength. PLE spectrum consists of three main peaks at 388 nm ($^6$H$_{5/2}$ to $^4$P$_{7/2}$), 449 nm ($^6$H$_{5/2}$ to $^4$P$_{7/2}$), and 487 nm ($^6$H$_{5/2}$ to $^4$I$_{11/2}$) [22]. The intensity of the PLE peak at 449 nm is highest. Figure 6 shows the PL of Ba$_3$Y$_{0.97}$(BO$_3$)$_2$:0.03Sm$^{3+}$ under 449 nm excitation. At 449 nm excitation, the PL spectra show three emission peaks centered at 590 nm, 644 nm, and 651 nm which are due to intra 4f shell transitions from excited level $^4$G$_{5/2}$ to ground level $^6$H$_{5/2}$, $^6$H$_{7/2}$, $^6$H$_{9/2}$ of...
Sm$^{3+}$ ions, respectively [23]. The broadband in the region 630-660 nm well matches with the absorption spectra of Pr. Thus, Ba$_3$Y$_{0.97}$(BO$_3$)$_3$: 0.03Sm$^{3+}$ phosphor can be used to modulate plant growth. The peak at 590 nm corresponding to the $^4$G$_{5/2}$ to $^6$H$_{5/2}$ transitions is magnetic dipole transition and does not affect by crystal field. The peak at 644 and 651 nm were related to the $^4$G$_{5/2}$ to $^6$H$_{9/2}$ is electric dipole transitioning and dependent on the crystal field. Mostly, the “Intensity of electric dipole transition to the intensity of Magnetic dipole transition” is used to determine the symmetry of local surroundings of Sm$^{3+}$ in the crystal [16,24,25]. It is found that that the “Ratio of the Intensity of the Electric to Magnetic Dipole Transition is less than one”, which represents that the Sm$^{3+}$ ions have occupied the symmetry position in the host crystal lattice. The emission spectra of Ba$_3$Y$_{0.97}$(BO$_3$)$_3$: 0.03Sm$^{3+}$ is also recorded under excitation at 388 nm, as shown in figure 7. The peak shape of all the samples was the same except noticeable change in intensity of peaks at 590 nm and 644 nm. To study the phenomena of concentration quenching in Ba$_3$Y$_{1-x}$(BO$_3$)$_3$: xSm$^{3+}$ (x= 0.01, 0.02, 0.03, 0.04, 0.05), the emission spectra are recorded at 449 nm excitation wavelength. PL spectra of Ba$_3$Y$_{1-x}$(BO$_3$)$_3$: xSm$^{3+}$ phosphors are shown in figure 8. It can be seen from fig. 8 that P-L intensity increases with an increase in the Sm$^{3+}$ ion concentration. The optimum Photo-Luminescence intensity is noticed for x=0.03, and beyond this concentration quenching followed. The probable reason of concentration quenching is increase in non-radiative transitions. The variation in the intensity with Sm concentration is shown in figure 9.

![Figure 5. PLE of Ba$_3$Y$_{0.97}$(BO$_3$)$_3$: 0.03Sm$^{3+}$ at room temperature](image.png)
Figure 6. PL emission spectra of Ba$_3$Y$_{0.97}$(BO$_3$)$_3$:0.03Sm$^{3+}$ at room temperature

Figure 7. PL of Ba$_3$Y$_{0.97}$(BO$_3$)$_3$:0.03Sm$^{3+}$ at room temperature
Figure 8. PL of $\text{Ba}_3\text{Y}_{1-x}(\text{BO}_3)_3$: $x\text{Sm}^{3+}$

Figure 9. Variation in PL intensity with Sm ion concentration

Figure 10 and 11 represent the CIE chromaticity coordinates & color gamut diagram of $\text{Ba}_3\text{Y}_{0.97}(\text{BO}_3)_3$:0.03$\text{Sm}^{3+}$ phosphor. The “CIE coordinates” of the phosphor $\text{Ba}_3\text{Y}_{0.97}(\text{BO}_3)_3$:0.03$\text{Sm}^{3+}$ for fixed concentration of $\text{Sm}^{3+}$ at 449 nm and 388 nm excitation were computed. The “CIE coordinates for spectra” observed under 449 nm and 388 nm excitation were determined to be (0.722, 0.277) and (0.602, 0.396), respectively. The “CIE coordinates” under excitation at 449 nm fall in the deep-red region. These phosphor-compounds can be excited by NUV and blue light, so can be used to fabricate the LEDs.
4. Conclusions

$\text{Ba}_3\text{Y}_{1-x}\text{(BO}_3\text{)}_3:x\text{Sm}^{3+}$ phosphors were synthesized by modified solution combustion route. XRD pattern confirmed the $\alpha$-$\text{Ba}_3\text{Y(BO}_3\text{)}_3$ structure of synthesized phosphors. The microstructures confirmed the formation of agglomerated particles with the average size in sub-micrometer range. It was observed that under excitation at 449 nm, PL spectrum consisted of highly intense peak at 644 nm, low-intensity peak at 589 nm, 651 nm and at 690 nm, while excitation at 388 nm, PL spectrum consisted of highly intense peak at 589 nm and low intensity line at 644 nm and 652 nm. Thus, by
changing the excitation wavelength, the color of emission changed from pure red to radish orange. It is color-tunable phosphor under photoluminescence excitation at two different wavelengths. In addition, the emission spectra of the prepared phosphors correspond to the absorption spectra of P_α phytochrome. The maximum Photoluminescence intensity was found for 3 mol% of Sm^{3+} ions. The CIE – chromaticity coordinates also fall in the red region. Also, the emission spectra of the presented phosphors correspond to the absorption spectra of P_α phytochrome. The emission of phosphors in the Red region under blue excitation makes them suitable candidates for ‘Red’ light-emitting diodes for “In-house plant applications”, “Indoor plant gardening”.

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