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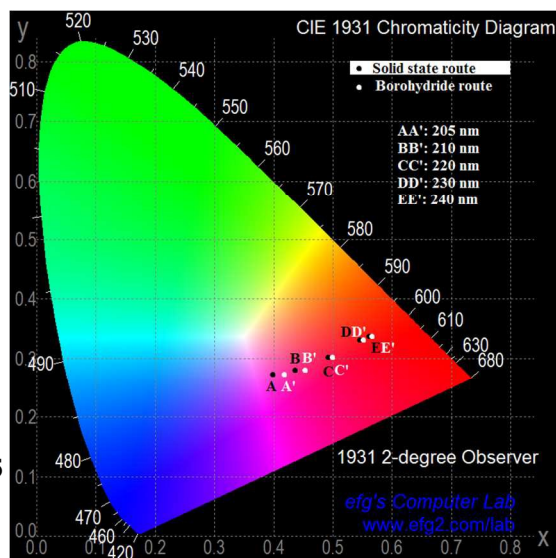
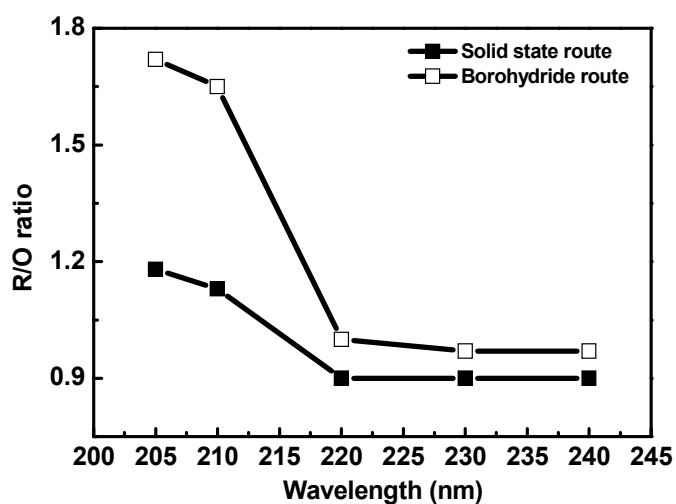
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Graphical Abstract



Text

Borohydride synthesized Eu^{3+} -doped YBO_3 exhibited better color purity and chromaticity co-ordinates as compared to phosphors derived from solid state route.

COMMUNICATION

Borohydride synthesis strategy to fabricate YBO₃:Eu³⁺ nanophosphor with improved photoluminescence characteristics

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This paper investigates for the first time the use of sodium borohydride (NaBH₄) as a boron source as well as a precipitating agent for successfully preparing high temperature stable YBO₃:Eu³⁺ nanophosphor. Moreover, the potential of this unique borohydride synthesis strategy is compared with conventional boric acid based solid-state route in terms of phase stability, morphology and photoluminescence characteristics. The novel synthesis approach adopted here renders a high temperature stable phase pure YBO₃:Eu³⁺ nanophosphor at 1200 °C with nearly spherical dumb-bell shaped particles in the range of ~ 200 nm to 700 nm and exhibits improved color purity when compared to the irregular polyhedral shaped (size ~ 5 μm) YBO₃:Eu³⁺ phosphor prepared by conventional solid-state method. Color purity, determined in terms of R/O ratio, of borohydride YBO₃:Eu³⁺ nanophosphor was found to be 1.72 for the near vacuum ultra-violet (VUV is characterized with wavelength shorter than 200 nm) wavelength of 205 nm, which gradually decreases with increase in excitation wavelength. It has never been reported that the color of YBO₃:Eu³⁺ phosphors can be tuned from pink to reddish-orange. The chromaticity coordinates revealed evidently that the YBO₃:Eu³⁺ phosphor emission is tunable by simply adjusting the excitation wavelengths. In addition to providing spectroscopic data the reason for better color purity and tenability of chromaticity coordinates are also accredited in this work.

YBO₃:Eu³⁺ phosphor has garnered immense focus owing to its strong photoluminescence intensity, high ultraviolet transparency and exceptional optical damage threshold as well as its prospective utilization in a myriad of applications spanning from flat display panels, white light emitting diodes to Hg free fluorescent lamps [1-3]. Numerous synthesis

methods such as sol-gel [4], solvothermal [5], co-precipitation [6, 7], hydrothermal [8, 9] and spray pyrolysis [10] have been developed for the formation of YBO₃:Eu³⁺ phosphor. However, almost all of these syntheses have made use of boric acid (H₃BO₃) as a boron source. The use of tributyl borate (C₁₂H₂₇BO₃) as a boron source has also been investigated [11]. Nevertheless, the results are not better than those obtained by boric acid. A notable point is that when the stoichiometric ratio of boric acid is maintained, phase purity is hardly achieved. Even there have been reports on the use of excess boric acid (~100% excess) to form phase pure YBO₃ [12]. This demonstrates the difficulty in obtaining phase purity of the phosphor. An impurity phase Y₃BO₆, which develops at higher temperatures, has been accounted for a drastic decrease of the photoluminescence intensity [13]. Besides, the color purity (which is generally assessed by R/O ratio) associated with YBO₃:Eu³⁺ phosphor has been a cause of concern. The R/O ratio is strongly dependent on the particle size of the phosphor. Further, the particle size can be tuned to a smaller dimension by adopting a novel synthesis approach. Syntheses strategies employed for the phosphor preparation aim towards improving the color purity and chromaticity of YBO₃:Eu³⁺ phosphor [14-16].

Our approach allows accomplishing this goal by means of a unique synthesis strategy for the production of high temperature stable phase pure YBO₃:Eu³⁺ along with an improvement in the color purity and chromaticity. A synthesis strategy based on the inclusion of sodium borohydride (NaBH₄), both as a boron source as well as a precipitating agent, is reported here. To the best of our knowledge, there have been no reports on the room temperature fabrication of YBO₃:Eu³⁺ phosphor using only NaBH₄. In the work

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described in this paper the potential of an apparently innovative borohydride synthesis approach has been justified by carrying out a detailed analysis of phase stability, morphology, photoluminescence, color purity and chromaticity. This kind of sodium borohydride based controlled precipitation route reported here puts forth a new approach to attain the nano sized $\text{YBO}_3:\text{Eu}^{3+}$ phosphors. In addition, a comparison was drawn with regards to boric acid based conventional solid-state derived $\text{YBO}_3:\text{Eu}^{3+}$ phosphor.

Borohydride synthesis through precipitation technique was adopted to prepare 10 mol % Eu^{3+} -doped YBO_3 phosphor material. Analytical grade (99.9% pure) reagents of yttrium oxide (Y_2O_3) and europium oxide (Eu_2O_3) were used as the starting materials. Appropriate amounts of these two materials are dissolved in hydrochloric acid (HCl) to form a precursor solution. Borohydride reaction was conducted at room temperature with drop wise addition of appropriate amount of aqueous NaBH_4 to the above precursor solution, with constant stirring using a magnetic stirrer. At a pH of ~ 10 , the precipitates were formed and then were washed several times with distilled water to remove unwanted products. After washing, the precipitate was dried and then calcined at 1200°C for 1h. For the sake of comparison, the conventional solid-state method was also employed to prepare the $\text{YBO}_3:\text{Eu}^{3+}$ phosphor with same concentration. The appropriate amount of Y_2O_3 , Eu_2O_3 and H_3BO_3 were mixed properly and calcined at three different temperatures (500°C , 1000°C and 1200°C for 1h), with an intermediate grinding step followed after each heat treatment. Phase analysis was carried out using X-ray diffractometer (Rigaku Ultima-IV X-Ray Diffractometer) with $\text{Cu K}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$). The morphology of the prepared samples was studied by Field emission scanning electron microscopy (FESEM) (Nova Nano SEM/FEI 450). The luminescence spectra were taken for excitation wavelengths of 205 nm, 210 nm, 220 nm, 230 nm and 240 nm with the help of F-7000 FL spectrophotometer.

X-ray diffraction patterns of $\text{YBO}_3:\text{Eu}^{3+}$ phosphor materials prepared using borohydride and solid-state method are presented in Fig. 1.

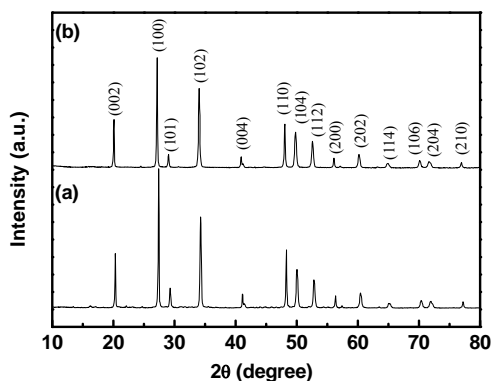


Fig. 1: XRD patterns of calcined (1200°C) $\text{YBO}_3:\text{Eu}^{3+}$ phosphors prepared using (a) conventional solid-state and (b) borohydride method.

All the peaks of both XRD patterns are well indexed with phase pure YBO_3 , as per the JCPDS file number: 16-

0277. It is notable to observe that the YBO_3 phase, by the borohydride route, was stable at a high temperature of 1200°C . Most prevalent Y_3BO_6 impurity phase was not observed up to 1200°C , which is a significantly higher temperature than the earlier reports for the formation of the Y_3BO_6 impurity phase^[13, 17]. The crystallite size of borohydride synthesized $\text{YBO}_3:\text{Eu}^{3+}$ phosphor found to be $\sim 47 \text{ nm}$, and was smaller than the solid-state derived phosphor (62 nm).

FESEM micrographs of $\text{YBO}_3:\text{Eu}^{3+}$ phosphor materials prepared using solid-state and borohydride methods are shown in Fig. 2 (a) and (b) respectively. In case of the solid-state route, clustering of polyhedral crystals form irregular shaped particles of size $\sim 5 \mu\text{m}$. On the contrary, morphology of $\text{YBO}_3:\text{Eu}^{3+}$ particles prepared by borohydride route exhibits fine dumb-bell shaped particles which may have been formed due to high temperature induced coarsening of finer spherical crystallites. The coarsening rate is reasonably low, which is evident by only necking of spherical particles. Even after high temperature treatment, the particles aggregate is fairly minimal within a size in the range of 200 nm to 700 nm .

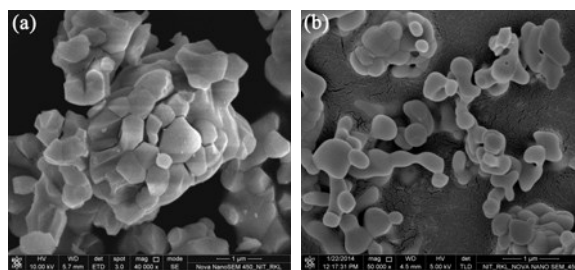


Fig. 2: FESEM micrographs of calcined (1200°C) $\text{YBO}_3:\text{Eu}^{3+}$ phosphors prepared using (a) conventional solid state and (b) borohydride method.

Emission spectra of $\text{YBO}_3:\text{Eu}^{3+}$ phosphor prepared using two methods are compared at an excitation wavelength of 205, 210, 220, 230 and 240 nm and is shown in Fig. 3. The major emissions are at 595 nm corresponding to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition and 614 nm and 630 nm corresponding to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition. The transition of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (red emission) is due to the typical electric dipole transition, and the transition of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ (orange emission) is attributed to the magnetic dipole transition^[1]. It is very clear that the luminescence intensity of the phosphor particles corresponding to the solid-state method of preparation is high, which is in striking contrast with the behavior of the particles prepared using the borohydride route, that demonstrate lower luminescence intensity. This is ascribed to the size of the particles, which is towards the lower range in the nanometer scale for the phosphor particles of the borohydride route. For plasma display panels (PDPs), poor color purity hampers the use of this phosphor, which corresponds to the fact that the intensity of red emission of $\text{YBO}_3:\text{Eu}^{3+}$ is lower than that of the orange one^[18]. Color purity is denoted as R/O ratio [$I({}^5\text{D}_0 \rightarrow {}^7\text{F}_2)/I({}^5\text{D}_0 \rightarrow {}^7\text{F}_1)$] and is calculated by considering the sum of integral intensity of red emission peaks observed at 614 and 630 nm for contribution of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition. From

Fig. 3, it seems that at lower excitation wavelengths, the color purity of borohydride-derived phosphor is higher than the solid-state derived phosphor. This can be succinctly expressed by means of the variation of R/O ratio with the excitation wavelength as revealed in Fig.4.

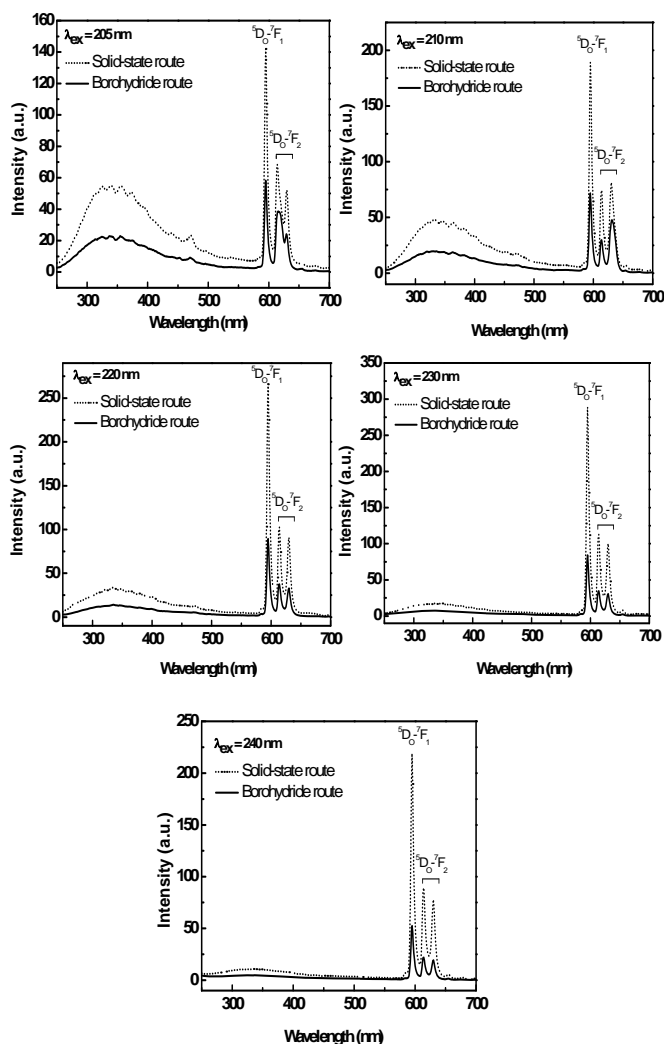


Fig. 3: Comparison of the emission spectra of $\text{YBO}_3: \text{Eu}^{3+}$ phosphor prepared via two methods.

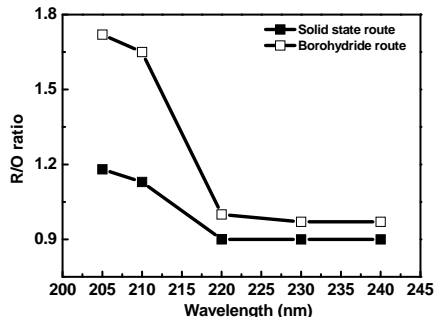


Fig. 4: Excitation wavelength dependent R/O ratio of $\text{YBO}_3: \text{Eu}^{3+}$ phosphor prepared via two methods

In both of the syntheses routes, the R/O ratio changes with excitation wavelengths. But, comparison of the two syntheses procedures accredits the fact that the phosphor

prepared using borohydride method has a better R/O ratio than the solid-state route. The R/O ratio is almost constant in the wavelength region of 220 nm to 240 nm with a value of 0.98 and 0.90 for borohydride and solid-state derived sample, respectively. Another noticeable point is that there is a steep rise in R/O ratio in the shorter wavelength region near VUV range (i.e. 205 and 210 nm). Even in that case, the values are higher (1.72) for the borohydride-derived phosphor, which is favorable for use in PDPs. The higher R/O ratio for borohydride-derived phosphor may be due to the smaller particle size of $\text{YBO}_3: \text{Eu}^{3+}$. Also, there is no direct correlation between size and color purity^[18]. In fact, the surface disorder associated with smaller particle size is responsible for the change in R/O values. As a result of smaller particle size, the crystal field environment of europium ions on the surface of particle is of higher complexity than the interior^[19]. In addition, the europium concentration on the surface and the interior of nano-sized phosphor is different. Higher disordered nature lowers the site symmetry on the surface and this lower site symmetry is not maintained towards the interior of the particle. The contribution of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is more prominent if the site symmetry is lower and thus leads to higher R/O ratio in near VUV range (205 or 210 nm), as VUV radiation penetrates only a part of the nanoparticle surface. However, contribution of both $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition lead to a decrease the R/O ratio in UV range (220 to 240 nm), as UV radiation penetrate through the particle. So, $\text{YBO}_3: \text{Eu}^{3+}$ phosphor prepared by our novel method exhibits a better R/O ratio in UV range and considerably higher R/O ratio in near VUV range as compared to solid-state derived phosphor. The observed value of R/O ratio is still higher than the reported value obtained via adopting various solution-based syntheses by modifying different parameters^[20, 21].

The commission International de l'Eclairage (CIE) 1931 XY chromaticity coordinate graph (XY diagram) of the borohydride synthesized nano-sized $\text{YBO}_3: \text{Eu}^{3+}$ and conventional solid-state derived bulk phosphor upon different excitation wavelengths are compared in Fig. 5. The CIE 1931 graph contains triangle of R (red), G (green) and B (blue) and the position of a color in the diagram is called chromaticity point of the color. The black and white dot corresponds to solid-state and borohydride derived $\text{YBO}_3: \text{Eu}^{3+}$ phosphor, respectively. With increase in excitation wavelength, the emitting color shifts from pink to reddish orange in both the cases. Such kind of color tuning has never been explored in $\text{YBO}_3: \text{Eu}^{3+}$ system, although the color tuning in other phosphor materials has been assessed^[22-24]. In general, the CIE coordinates were calculated by taking into account the visible range (400-700 nm) of the emission spectrum as shown in Fig. 3. The emission spectra consists of a broad peak starting from 250 nm to 450 nm centering at 350 nm and three sharp peaks at 595 nm, 614 nm and 630 nm. The broad nature of peak is mainly due to the contribution of the host i.e. borate group ions, whereas, the three sharp peaks are a result of the contribution of activator i.e. europium ions^[18, 25, 26]. The emission mechanism of the phosphor under 205 and 210 nm is indirect emission because of energy transfer from the

host to activator^[26]. So, the contribution of the borate group ions comes to the fore on being excited by high-energy near-VUV radiation and as a result of which a conspicuous emission in 250–450 nm is observed. On the other hand, the activators are directly excited in case of UV radiation (220 nm to 240 nm) and the contribution of borate group is less due to which the intensity of emission in that particular region progressively decreases. This intensity difference manifests itself in the form of a change in the chromaticity coordinate positions in CIE diagram, which shows its position spanning from pink to reddish orange region. However, borohydride derived $\text{YBO}_3:\text{Eu}^{3+}$ phosphor shows a better chromaticity than solid-state derived phosphor, specifically at lower excitation wavelengths of 205 nm and 210 nm. Although, at higher excitation wavelengths (220, 230 and 240 nm), the chromaticity of borohydride-derived phosphor is comparable with the solid-state derived phosphor. Based on this study, it can be ascertained that tuning of the color intensity of $\text{YBO}_3:\text{Eu}^{3+}$ phosphors is possible. Efforts for improving the color purity and chromaticity of borohydride derived $\text{YBO}_3:\text{Eu}^{3+}$ phosphor are under progress.

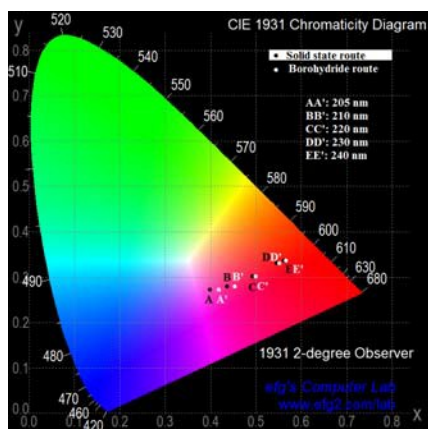


Fig. 5: Excitation wavelength variation chromaticity diagram for $\text{YBO}_3:\text{Eu}^{3+}$ phosphor synthesized by solid-state and borohydride method.

Conclusions

Spherical dumb-bell shaped $\text{YBO}_3:\text{Eu}^{3+}$ nanophosphor having particle size of 200 nm to 700 nm was successfully prepared by unique borohydride synthesis approach using NaBH_4 . This gives an affirmative and encouraging indication that the borohydride based novel method of synthesis provides for a higher temperature stability up to 1200 °C. The explicit potential of the borohydride strategy is to prepare $\text{YBO}_3:\text{Eu}^{3+}$ phosphors with superior characteristics in connection with the color purity described by R/O ratio. The higher R/O ratio (1.72) for near VUV wavelength (205 nm) in borohydride derived phosphor depends on the contribution of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, which is more prominent and may be owing to highly disordered surface with lower site symmetry. However, contribution of both $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition lead to a decrease in R/O ratio in UV range (220 to 240 nm). Color tuning from pink to reddish orange is possible for $\text{YBO}_3:\text{Eu}^{3+}$ phosphors by changing the excitation wavelengths from near VUV to UV range due to the

contribution of the host and the activator. The findings of the study suggest that this borohydride method is better than the conventional boric acid based solid-state method. Consequently, the borohydride synthesized spherical dumb-bell shaped $\text{YBO}_3:\text{Eu}^{3+}$ phosphor material could be quite feasible in the display and optics domain.

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