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Effect of partially replacement of Gd^{3+} ions on fluorescence properties of $YBO_3:Eu^{3+}$ phosphor synthesized via precipitation method

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The series of $(Y_{(1-x)}Gd_x)BO_3:_{0.01}Eu^{3+}$ phosphors was successfully synthesized by precipitation method. All phosphors were characterized by X-ray diffraction pattern (XRD) for crystalline structure and UV–vis, photoluminescence (PL) and decay curves measurements were carried out to characterize their optical properties. The PL emission spectra of $(Y_{(1-x)}Gd_x)BO_3:_{0.01}Eu^{3+}$ phosphors indicated that red–orange (595 nm) color could be well excited by 233 nm. The effect of x (Gd^{3+} ions) increases in $(Y_{(1-x)}Gd_x)BO_3:_{0.01}Eu^{3+}$ on PL properties has been examined. The results showed that increment of x molar concentration in $(Y_{(1-x)}Gd_x)BO_3:_{0.01}Eu^{3+}$ would lead to a outstanding enhancement of fluorescence intensity. The chromaticity coordinates (CIE) were calculated. The R/O ratio of the luminescence intensity of $^5D_0 \rightarrow {}^7F_2$ (red) to $^5D_0 \rightarrow {}^7F_1$ (orange) transitions were very well increases with the increasing percentage of Gd^{3+} ions in $(Y_{(1-x)}Gd_x)BO_3:_{0.01}Eu^{3+}$ phosphor.

1. Introduction

YBO_3 is a vaterite type material which is widely used as red phosphors for plasma display panels and Hg-free fluorescent lamps due to their ideal VUV absorption, stable physico-chemical properties and non-linear optical properties [1]. Also it is very well known that the YBO_3 possess wide band gap and high transparence characteristics. Hence, in the past few years, YBO_3 doped with different rare earth ions were discovered and studied for various applications such as fluorescent lamp, VUV absorption, and display devices. This is only because of their excellent efficiency, high color purity, very good refractory properties and good stability [2–4]. Till date many researchers tried to enhance the luminescence in YBO_3 host material by means of modification in synthesis or by changing the doping and co-doping in the cluster, where as Gd is always proposed to be a possible enhancer [5,6]. Most commonly conventional routes were adopted for synthesis [7–10]. But, the particle size of resulting material prepared by solid state method is in the range of few micrometers and in heterogeneity of as-prepared phosphors particle size. Therefore, there is need to synthesis of such a phosphors by which we get well defined and small nano-size materials [11]. However, there are lots of non conventional techniques available like co-precipitation [12], spray pyrolysis [13], sol–gel method [14] and combustion synthesis [15] and the advantages of these methods were controlling particle size, homogeneity, low cost, etc., as compare to the solid state reaction. But they have some drawback such as in spray pyrolysis process, hollow and highly porous particles are generated due to this structural defects can be produced, which lead to decrease in luminescence efficiency of the prepared phosphor. In sol–gel method, drying and annealing processes have to be slow and deliberate otherwise cracks and striations will appear in the samples and it is difficult to completely remove the residual hydroxyls from the phosphors [16]. Similarly in combustion synthesis, fuel and oxidizer is required and also it is very difficult to maintain the fuel/oxidizer ratio. In co-precipitation method drying and washing process is required, additionally it required precipitation agent.

Inspiring from the above discussions, the present work planned to study the PL properties of $(Y_{(1-x)}Gd_x)BO_3:_{0.01}Eu^{3+}$ phosphors synthesized by more efficient synthesis method known as modified precipitation method and it not required any precipitation agent. The synthesis through precipitation method is low cost, low temperature and it not required any other agent for initiation of process of synthesis and there is no need of drying and annealing but the only drawback associated with the method is to required soluble precursors. However, the method results in outstanding luminescent intensity phosphor, which is main accomplishment of the present work.

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2. Experimental

2.1. Synthesis

The phosphor $YBO_3:Eu^{3+}$ was prepared by slow evaporated precipitation method. The starting chemicals Y_2O_3 (99.99%, AR) and Eu_2O_3 (99.90%, AR) were mixed together in a china clay basin. A small quantity of deionized water of resistivity not less than18.2 MΩ-cm was added and paste was formed. HNO_3 was added drop by drop and under observation, mixture was heated slowly at 50 °C, till the paste dissolved completely. The solution was further heated to get excess of acid boiled off. Little quantity of double distilled water was again added. The resulting solution was considered as $Y(NO_3)_3$:Eu, to this soluble solution, H_3BO_3 (AR) dissolved in double distilled water were added drop by drop. The entire homogenous soluble solution was then placed on hot plate at 60 °C for slow evaporation of water. The dried precursor was finally crushed and heated at 900 °C to get white crystalline powder of $YBO_3:Eu^{3+}$. The same process was utilized in synthesis of all the samples, only the Y/Gd ratio was changed as per the formula $(Y_{(1-x)}Gd_x)BO_3:_{0.01}Eu^{3+}$. The complete process involved in the reaction was represented as a flow chart in Fig. 1.

2.2. Characterization of samples

The phase purities of $YBO_3:Eu^{3+}$ samples were studied using Rigaku miniflex II X-ray Diffractometer with scan speed of 2.000°/min and Cu Kα ($\lambda = 1.5406$ Å) radiation in the range 10–90°. The diffuse absorption spectra of solid sample were measured on Agilent Cary 7000 universal measurement spectrophotometer (UMS) with solids auto sampler. 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. The color chromaticity coordinates were obtained according to Commission International de I'Eclairage (CIE) using radiant imaging software.

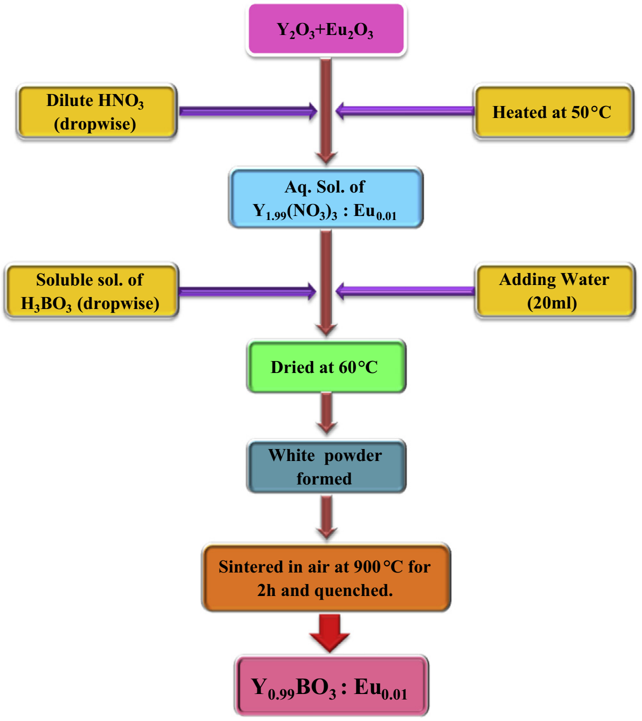

Fig. 1. Flow chart of $Y_{0.99}BO_3:_{0.01}Eu^{3+}$synthesized by precipitation method.

3. Results and discussion

3.1. Structural properties

The formation of the YBO_3 in the crystalline phase prepared by precipitation method was confirmed by XRD pattern as shown in Fig. 2. The XRD pattern for $YBO_3:Eu^{3+}$ agreed well with the standard data from ICDD file (00-016-0277). From the XRD pattern, the high intensity peaks at 20.16, 27.24, 34.11, 48.15, 49.19 and 52.68, which are corresponding to (002), (100), (102), (100), (104) and (112) respectively. The more significant and refined XRD pattern is represented in Fig. 2, where the background is subtracted from originally observed XRD pattern. The less background and high crystalline nature support the formation of desired $Y_{1.99}BO_3:_{0.01}Eu^{3+}$ phase. Also the XRD show that the formed material is completely crystalline and was in single phase, where $a = b = 3.778$ and $c = 8.810$ Å. The space group for YBO_3 is P63/m.

The XRD patterns of $(Y_{(1-x)}Gd_x)BO_3:_{0.01}Eu^{3+}$ phosphors as depicted in Fig. 3(A). When Gd^{3+} ions gradually increase in place of Y^{3+} ions, their XRD patterns significantly changes. In other word all peaks of $(Y_{(1-x)}Gd_x)BO_3:_{0.01}Eu^{3+}$ slightly shifted toward lower 2θ angle with same crystal structure (dotted lines shows peak shifting difference in Fig. 3(A)). The ionic radius of Y^{3+} is 0.9 pm, Gd^{3+} is 0.94 pm and Eu^{3+} is 0.95 pm for six fold coordination. Therefore, it is expected that the doped Eu^{3+} and Gd^{3+} ions has replaced Y^{3+} ions in YBO_3 lattice [17]. However, when the molar concentration of Gd^{3+} ion in $(Y_{(1-x)}Gd_x)BO_3:_{0.01}Eu^{3+}$ was zero, the diffraction pattern is of course the same as that of $YBO_3:_{0.01}Eu^{3+}$ except shifting of all peaks at lower 2θ angle (Expanded shifting view of main XRD peaks as shown in Fig. 3(B)). When the molar concentration of Gd^{3+} ions increases, the diffraction peaks were move to the lower 2θ angle and when Gd^{3+} ions completely replaced by Y^{3+}ions, the material crystallizes into $GdBO_3:_{0.01}Eu^{3+}$ phase. The XRD pattern of $Gd_{1.99}BO_3:_{0.01}Eu^{3+}$ phosphor indicates a pure phase of the standard $GdBO_3$ and all the peaks were in good agreement with the ICDD: 00-013-0483. Also the XRD shows that the formed material was completely crystalline and was in single phase, where $a = b = 3.829$ and $c = 8.890$ Å.

The average crystallite size of $Y_{1.99}BO_3:_{0.01}Eu^{3+}$ phosphor determined from Debye–Scherrer formula [18]. In Fig. 4, it is clearly shows that the particle size of $YBO_3:Eu^{3+}$ was greater than $GdBO_3:Eu^{3+}$. There was a simultaneous increase in crystalline size with increases in molar concentrations of Gd^{3+} ions up to 0.5. Beyond, increasing the molar concentration of Gd^{3+} ion up to 0.7, particle size decreases. The minimum particle size observed at 1.0 M concentration of Gd^{3+} ions i.e. $GdBO_3:Eu^{3+}$. Conversely, lattice stains shows opposite behavior as we obtained in case of particle size reduction.

3.2. UV–Visible spectroscopy

The UV–vis analysis of $(Y_{(1-x)}Gd_x)BO_3:Eu^{3+}$ phosphors are shown in inset of Fig. 5 was carried out with a view to explore their optical properties. The spectra of $(Y_{(1-x)}Gd_x)BO_3:Eu^{3+}$ phosphors shows strong absorption in the UV spectral region and with some weak peaks in the IR region. The variation of Y^{3+} to Gd^{3+} ratio in $(Y_{(1-x)}Gd_x)BO_3:Eu^{3+}$ strongly affects the structure of host lattice and it was clearly observed from the UV-analysis as the absorption edges are changing with the Y^{3+} to Gd^{3+} ratio. Also, the main absorption peak changed from sample to sample, this strong change in absorption may ascribe to change in crystal structure. This discussion supported by XRD analysis. According to Tauc [19], the optical band gap