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Aldo-keto synthesis effect on Eu^{3+} fluorescence in YBO_3 compared with solid state diffusion

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Abstract: The red-orange emitting phosphor $YBO_3:Eu^{3+}$ was prepared by aldo-keto method and solid state diffusion. Aldo-keto method implied to decrease the processing time and heating temperature. The red-orange emitting phosphor was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), as well as emission and excitation photoluminescence spectra recorded at room temperature. The result of aldo-keto method showed that the phosphor $YBO_3:Eu^{3+}$ could be obtained at 900 °C in less time ~60% as compared to solid state diffusion (SSD). The material showed that the strongest emission peak at 595 nm under excitation at 233 nm was only due to forced magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+} ions. Significantly, the emission intensity of $YBO_3:Eu^{3+}$ phosphor prepared by aldo-keto method was relatively higher as compared to that obtained by the solid state diffusion.

Keywords: aldo-keto method; yttria; europium; optical materials; photoluminescence (PL); rare earths

In the past few years, rare earth doped YBO_3 phosphor were intensively studied for modern applications in luminescence field such as VUV absorption, plasma display panels, Hg-free fluorescent lamps, etc.[1,2]. Many researchers studied the synthesis of yttrium borate phosphor across the globe, due to the wide band gap and transparence characteristics, trying to enhance their fluorescence intensity. Therefore, researchers tried to use various synthesis routes. Wang et al. synthesized $YBO_3:Eu^{3+}$ co-doped with some ns^2-type ions using solid-state reaction for red phosphor for UV and VUV application[3]. Park et al. synthesized $YBO_3:Eu^{3+}$ phosphor by modified ultrasonic spray pyrolysis under optimum temperature at 1200 ºC for plasma display panel (PDP) application[4]. Jung et al. modified the luminescent properties of $YBO_3:Eu^{3+}$ synthesized through spray pyrolysis with sintering temperature of 1100 ºC for 3 h to enhance luminescent intensity of red phosphor under vacuum ultraviolet excitation[5]. Red-orange emitting Eu^{3+} doped YBO_3 phosphors have been prepared by solid state synthesis by Balakrishnaiah et al.[6]. In this study, solid state reaction was performed at 1100 ºC and Li doping was used for the charge conjugation to improve intensity of as-synthesized materials. The solid state method was employed for the synthesis of $YBO_3:Eu^{3+}/Tb^{3+}$. Luminescence material was explored for lamp phosphor application by Gao et al. at relatively low synthesis temperature but with more time[7]. Sato et al. synthesized the $YBO_3:Ce^{3+},Tb^{3+}$ luminescence materials by solid state reaction at sintering temperature of 1100 ºC[8]. Dubey et al. studied photoluminescence properties of $YBO_3:Eu^{3+}$ phosphor under UV radiation synthesized by solid state method with stepwise annealing temperatures of 500, 1000 and 1250 ºC for 1 h[9].

Inspired from the above discussion, we planned to study the luminescent properties of $YBO_3:Eu^{3+}$ phosphor synthesized using solid state diffusion and aldo-keto methods. To the best of our knowledge and from the literature survey, the synthesis of $YBO_3:Eu^{3+}$ by solid state diffusion method was reported by many researchers and in present work also, which required high temperature. However, the synthesis through aldo-keto method was processed at low temperature and less time consuming and resulted in high luminescent intensity phosphor, which is the main accomplishment of the present work.

1 Experimental

1.1 Solid state diffusion

The precursor Y_2O_3 (99.99%, AR) Eu_2O_3 (99.90%, AR) and H_3BO_3 (AR) were mixed thoroughly in a mortar. The resultant mixture was transferred to an alumina crucible and oven dried at 40 ºC. The mixture was heated in a resistive furnace at different elevated temperatures (400, 600, 800 and 1000 ºC) for 2 h at each step with intermittent grindings. The white powder of $YBO_3:Eu^{3+}$ so obtained was used for characterization.

It was well discussed by the researchers that SSD not only needs highly sophisticated equipment but also pro-

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duces non-uniform particles due to high temperature diffusion. The intermediate grinding required for the fusion of materials produces lots of physical defects and increases the time of reaction[10]. The physical defects produced during the reaction affect the efficiency of phosphor. To overcome the possible drawbacks of solid state diffusion method, we have tried aldo-keto method. The idea about this method originated from the glucose-fructose gel.

1.2 Aldo-keto method

The phosphor YBO_3:Eu^{3+} was prepared for the first time by a novel method of gelation named as aldo-keto gel method, which offers a comparatively low temperature route[11]. 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 double distilled water was added and paste was formed. HNO_3 was added drop by drop and mixture was heated slowly under observation to 50 ºC till the paste dissolved completely. The solution was further heated till the excess of acid was boiled off. A small quantity of double distilled water was again added and slowly evaporated to dryness. The resulting powder was $Y(NO_3)_3$:Eu, after that soluble solution of H_3BO_3 (AR) was added. The dried precursor was finally milled. Acetone (2 mol/L, AR) and benzaldehyde (2 mol/L, AR) were added to the nitrate. The pale brownish yellow mixture obtained was stirred continuously and slowly heated to 130 ºC. The mixture became dark brownish yellow and then dark reddish brown between 80 to 120 ºC with evolution of brownish gases. The process of gelation started at nearly about 130 ºC with the evolution of dark yellowish brown fumes. The mixture was then allowed to cool. Red gel was formed after cooling. It was further heated slowly to 300 ºC. Dark red foam was formed with evolution of yellowish brown fumes. On further slow heating, pyrolysis of foam was started at 450 ºC and shining black foam was formed at 600 ºC, which started burning from 900 ºC. Final product appears as white crystalline powder of YBO_3:Eu^{3+}.

1.3 Characterizations

The phase purities of YBO_3:Eu^{3+} samples were studied using a Rigaku miniflex II X-ray diffractometer with a scan speed of 2.000 (º)/min and Cu Kα (λ=0.15406 nm) radiation in the range from 10° to 90º. The photoluminescence emission (PL) and photoluminescence excitation (PLE) spectra were measured on a 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)[12].

2 Results and discussion

2.1 XRD patterns of YBO_3

The formation of the crystalline phase of as-prepared products of solid state diffusion and aldo-keto method was confirmed by X-ray diffraction patterns of YBO_3 (as shown in Fig. 1) to verify the phase purity and crystal structure. The X-ray pattern of both method samples indicated a pure phase of the standard YBO_3 and all the peaks were in good agreement with the ICDD file (00-016-0277). There were no additional peaks found as the concentration of Eu ion was increased to 5 mol.%. From the above discussion most of the researchers have reported in the literature that pure phase of YBO_3 could be achieved using solid state synthesis, which required more time for synthesizing. In this paper the YBO_3 sample was successfully prepared at 900 ºC by aldo-keto method in less time (~60%) as compared with solid state diffusion method. The XRD pattern for YBO_3:Eu^{3+} agrees well with the standard data from ICDD file (00-016-0277). The high intensity peaks i.e., 20.16, 27.24, 34.11, 48.15, 49.19, and 52.68 corresponding to (0 0 2), (1 0 0), (1 0 2), (1 0 0), (1 0 4) and (1 1 2) respectively in ICDD file shows exact matching with the XRD pattern of phosphor prepared by aldo-keto method. This agreement indicates that the phosphor 00-016-0277 has been successfully prepared by using the aldo-keto method. Also the XRD shows that the formed material was completely crystalline and is present as a single phase with hexagonal structure where a=b=0.3778 and c=0.8810 nm. The space group for YBO_3 is $P63/m$.

Fig. 1 shows XRD pattern of YBO_3 phosphor synthesized by solid state diffusion and aldo-keto method which exactly match with each other. It is observed that XRD pattern contains 6 prominent peaks between position 2θ=20°–60°. The average crystallite size was determined from XRD pattern using Scherrer formula[13]. From main 6 peaks, the average crystallite size of YBO_3

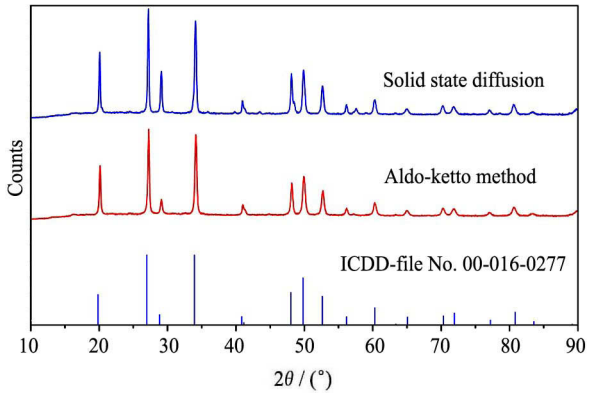

Fig. 1 XRD patterns of the YBO_3 phosphor synthesized by solid state diffusion and aldo-keto method