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NOVEL PREPARATION METHOD AND LUMINESCENT PROPERTIES OF Eu^{3+} DOPED YBO_3 PHOSPHOR UNDER VUV EXCITATION

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Abstract: Eu^{3+} doped yttrium borates were prepared by a novel low-temperature re-crystallization (RC) method. The effects of preparation techniques on the phase formation, morphologies and luminescent properties in VUV region were investigated. The use of the re-crystallization method in preparation lowered the reaction threshold temperature by c.a. 200°C. The results revealed that particle morphology and photoluminescence intensity under VUV region were largely dominated by the type of preparation method. Strong photoluminescence spectra were obtained at 592, 611 and 627 nm at excitations wavelengths 172 nm. The emission spectra are associated with the transitions from the excited $^5D_0$ level to the ^7F_J (J = 1, 2, 3, 4) levels of Eu^{3+} activators.

1 Introduction

Over the last few years, $YBO_3:Eu^{3+}$ has been recognized as one of the best commercial red phosphors for plasma display panels (PDP) and Hg-free fluorescent lamps due to its high vacuum ultraviolet (VUV) absorbency and extraordinarily high luminescent efficiency under VUV excitation [1-3]. Much attention has been focused on the research of $LnBO_3$ (Ln = rare earth and yttrium) due to their excellent luminescent properties of high vacuum ultraviolet (VUV) transparency, exceptional optical damage thresholds, and chemical and environmental stability [4–8]. Various methods have been used to prepare $LnBO_3$ phosphor materials, for example, conventional solid-state reaction [9-11], co-precipitation [12, 13], microwave heating [14], spray pyrolysis [15], sol-gel [12], combustion [16], and hydrothermal method [17–19]. The fabrication of phosphor materials with well controlled dimensionality, morphologies, phase purity, chemical composition and desired properties remains one of the most challenging issues. Commonly, the phosphor powders are prepared by conventional solid-state reaction at high temperature. Although simply operated, this method has several disadvantages including high-temperature processing, long calcination time and repeated

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milling and grinding. High calcination temperature for long time can make the phosphor particles easily agglomerated to form a particle block, therefore, milling and grinding are required to achieve desirable particle size [20]. However, the surface of phosphors suffers from damage in milling and grinding processes. Recent studies indicated that the penetration depth of VUV is about 100–200 nm [21], consequently, the surface damage resulting from grinding and milling processes will significantly degrade the luminescence properties of phosphors. Furthermore, due to the limitation of solid-state route, the resulting product prepared by this method is very difficult to achieve compositional homogeneity, and the doped ions are not able to be uniformly dispersed in the crystal lattice thus several impurities are more likely to be introduced and the luminescence efficiency is lowered. In order to improve the morphology and thus the luminescence property of $YBO_3:Eu^{3+}$ low temperature synthesis methods i.e. re-crystallization (RC) is investigated. The prepared phosphor is investigated under high-energetic VUV excitation using synchrotron radiation as a light source. The effect of the preparation condition on the VUV excited luminescence of the phosphors was notable.

2 Experimental

2.1. Re-crystallization Method

The phosphor $YBO_3:Eu^{3+}$ was prepared for the first time by a re-crystallization method; offering a comparatively low temperature route, higher controllability and easy to soluble are the primary advantages. 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 than 18.2 MΩ-cm was added to get a thick paste. To the thick paste, HNO_3 was added drop by drop. Then the mixture was heated slowly at 50°C, till the paste dissolved completely. The solution was further heated to get an excess of acid boiled off. Less 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 a hot plate at 60ºC for slow evaporation of water. The dried precursor was finally crushed and heated at 900ºC to get white crystalline powder of $YBO_3:Eu^{3+}$. The complete process involved in the reaction is represented as a flowchart in **Fig. 1**.

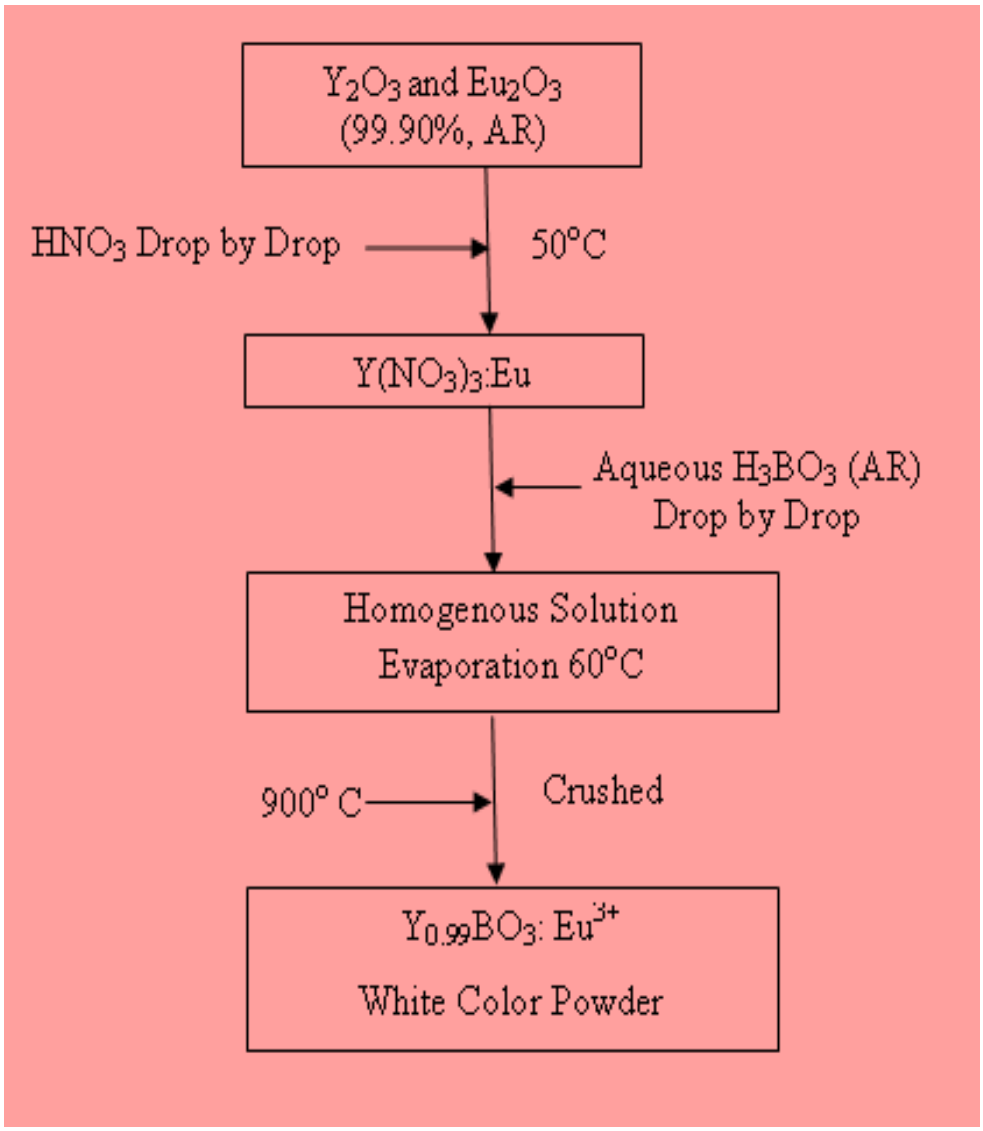

Fig. 1. Flow chart for synthesis of $Y_{0.99}BO_3:_{0.01}Eu^{3+}$ by Re-crystallization method.

2.3. Characterizations

The X-ray diffraction (XRD) pattern of host sample of $Y_{0.99}BO_3:_{0.01}Eu^{3+}$ was recorded on Rigaku MiniFlex diffractometer with scan speed 2000 deg/min. The morphology of the phosphor particles was studied by using Hitachi model S-4800 type-2 field emission scanning electron microscope and elemental analysis by Bruker EDS. The VUV spectra were recorded at Department of Physics S.G.B. Amravati University, Amravati by using remote access mode of Beamline 4B8 in Beijing synchrotron radiation facilities (BSRF) [22] under dedicated synchrotron mode (2.5 GeV, 150–60 mA). The vacuum in the sample chamber was about 1×10^{-5} mbar. The effects of the experimental set-up response on the relative VUV excitation intensities of the samples were corrected by dividing the measured excitation intensities of the samples with the excitation intensities of sodium salicylate measured

simultaneously in the same excitation conditions. The region of excitation spectra was from 100 nm to 300 nm and the emission spectra recorded under 147 and 172 nm excitation.

3. Result and Discussion

3.1. XRD analysis

The formation of the crystalline phase in products prepared by the Re-crystallization method was confirmed by X-ray diffraction patterns of YBO_3 shown in **Fig. 2.** The XRD pattern for YBO_3:Eu^{3+} agrees well with the standard data from ICDD file (00-016-0277). The peaks from the XRD pattern of phosphor prepared by Re-crystallization form at 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, show exact matching with standard ICDD file data. Also the XRD show that the formed material was completely crystalline and in a single phase with a hexagonal structure where a = b = 3.778 and c = 8.810 Å. The space group for YBO_3 was P63/m. It is observed that XRD pattern contains 6 prominent peaks between position 2θ= 20°-60°. The average crystallite size, determined from XRD pattern using Scherrer formula. From main 6 peaks, the average crystallite size of YBO_3 by using Scherrer's formula estimated 198 nm for solid state diffusion and 179 nm for aldo-ketto method [14].

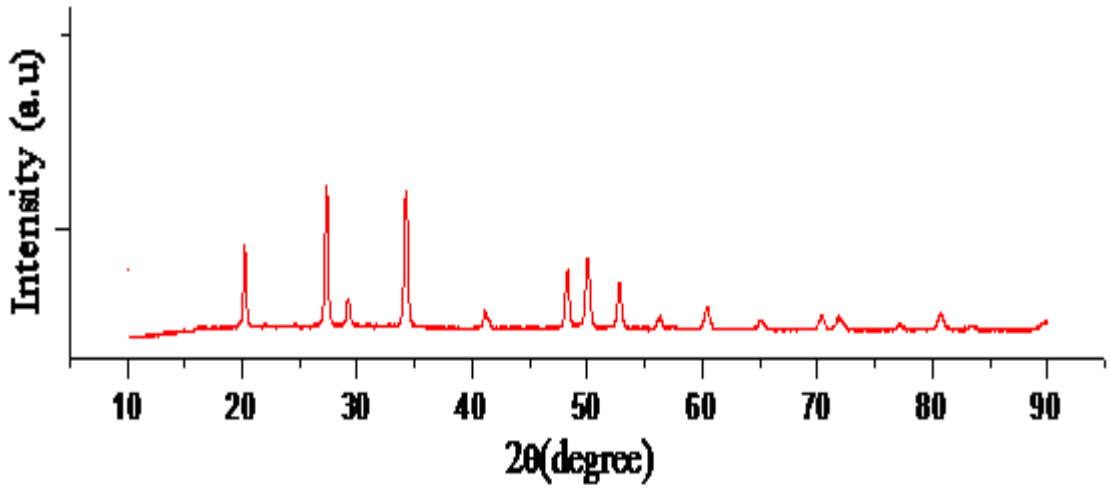

Fig. 2. XRD pattern for $Y_{0.99}BO_3$:$_{0.01}Eu^{3+}$.

3.2. MORPHOLOGY

The spectra obtained during EDX studies were used for carrying out the quantitative analysis. Fig. 3 shows the EDX spectrum of YBO_3:Eu^{3+} particles synthesized by the Re-crystallization method and annealed at 900 ^oC for 2h. The EDX spectrum of YBO3:Eu^{3+} phosphor shows the presence of yttirium, boron, oxygen and europium. EDX quantitative micro analysis indicates the presence of 1% europium in YBO_3:Eu^{3+} phosphor.

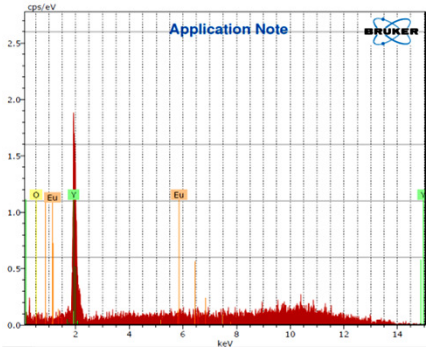

Fig.3. EDX spectrum of $YBO_3:Eu^{3+}$ synthesized by Re-crystallization method and annealed at 900 ^{O}C.

The SEM images of YBO3 crystals synthesized by the Re-crystallization method are shown in Fig. 4. As can be seen, YBO3 particles synthesized show the uniform shape, they are agglomerates of little spheres with the size range of 1 μm.

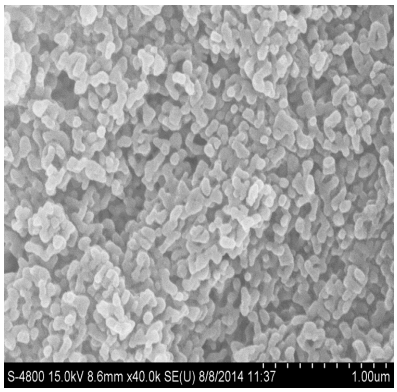

Figure. 4. SEM image of the $YBO_3:Eu^{3+}$ phosphor synthesized by Recrystallization method.

3.3. Luminescence spectra under VUV excitation

The photoluminescence excitation and emission spectra in the VUV range using synchrotron radiation for Eu^{3+} doped YBO_3 samples are shown in **Figs. 5 and 6**, respectively.

3.3.1. Excitation spectra.

The photoluminescence excitation spectra in the VUV range using synchrotron radiation for the Yttrium borates doped with Eu^{3+} are displayed in **Figure 5**.

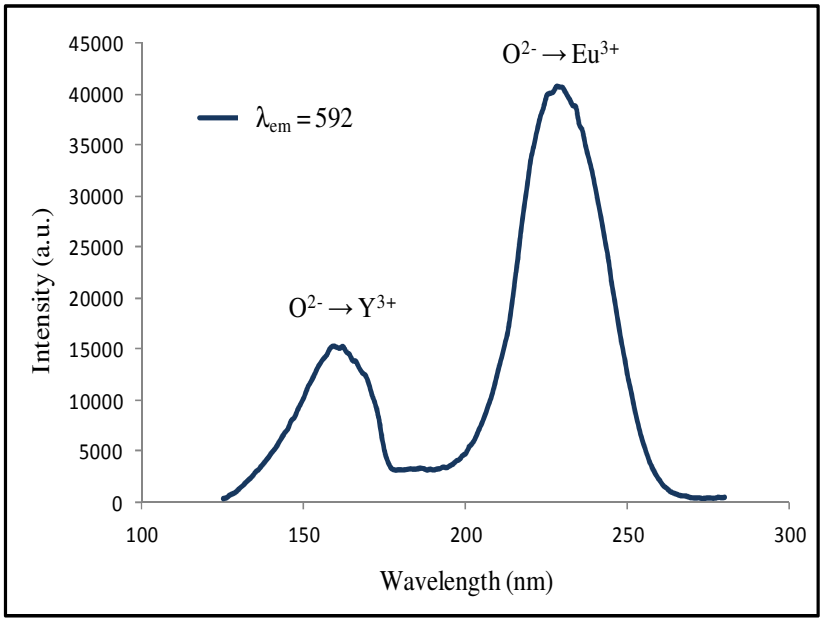

Fig.5. excitation spectra of $Y_{0.9}Eu_{0.01}BO_3$ (monitoring wavelength (592 nm) by using synchrotron radiation. The relative intensities are arbitrary.

The excitation spectra measured for $Y_{0.9}Eu_{0.01}BO_3$ upon Eu^{3+} emission at 610 nm for the sample prepared by Recrystallization method is shown in Fig. 5. There are two main broad excitation peaks, one is ascribed to absorption of the host lattice that overlapped with CT band of $O^{2-} \rightarrow Y^{3+}$ and the second is assigned to $O^{2-} \rightarrow Eu^{3+}$ charge transfer [23].

3.3.2. Emission spectra.

Figure 6 shows the emission spectrum of Eu^{3+}-doped YBO_3 excited by 147 nm and 172 nm respectively. The emission spectrum of Eu^{3+}-doped YBO_3 prepared by low temperature method i.e. re-crystallization (RC) shows intense emission sharp peaks, associated with the transitions $^5D_0 \rightarrow F_J$ (J=1, 2, 3, 4) characteristic for Eu^{3+} ions, are observed. The intensity ratio of $^5D_0 \rightarrow {}^7F_1$ to $^5D_0 \rightarrow {}^7F_2$ bands varies with the changing of excitation. It is interesting to note that the emission intensity of Eu^{3+}-doped YBO_3 crystals prepared by the recrystallization method is about 3.5 times as much as that by the other methods. The emission intensity of Eu^{3+}-doped YBO_3 crystals prepared can be explained by considering the morphology of crystals and the phase formation during the processes. The particles of the YBO_3 prepared via the explained method were less agglomerated and the extent of crystallization was higher with uniformity in shape and size (Fig.4).

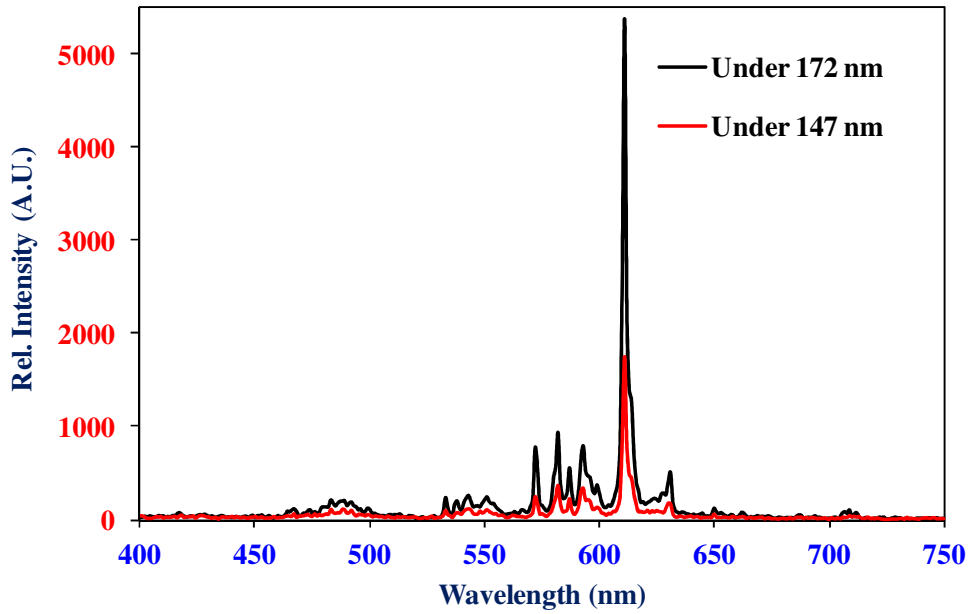

Fig.4. The emission spectra of Eu^{3+}-doped YBO_3 crystals synthesized Re-Crystallization (RC) method (λ_{ex}=147 nm and 172 nm)

Conclusions

Eu^{3+}-doped YBO_3 material was successfully prepared through a Re-Crystallization (RC). The emission intensity of the Eu^{3+} ion in YBO_3 material prepared via low temperature methods i.e. Re-Crystallization (RC) are higher than those obtained from the high temperature methods i.e. Solid State Diffusion (SSD) and Solution Combustion (SC) reported, due to the high crystallization and the uniform morphology. Predominantly the Re-Crystallization technique has some advantages over other methods described, in preparing the YBO_3 phosphors based on the results of our research. Considering the reaction conditions and luminescent properties of the products, the low temperature methods and specifically Re-Crystallization is promising process for the preparation of the phosphor materials.

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