Research Article

A Potential Candidate for Lamp Phosphor: Eu^{3+} Activated $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7$

K. A. Koparkar, N. S. Bajaj, and S. K. Omanwar

Department of Physics, SGB Amravati University, Amravati 444602, India

Correspondence should be addressed to N. S. Bajaj; nsb.0208@yahoo.com

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The novel phosphor $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7$ doped with europium is studied for its photoluminescence properties. The studies show that the phosphor gives strong red emission (PL) at 613 nm related to $^5\text{D}_0$ - $^7\text{F}_2$ transition of Eu^{3+} under the 260 nm excitation (PLE) related to the charge transfer (CT) from the 2p orbital of the O^{2-} ions to the 4f orbital of Eu^{3+} ions with CIE coordinates ($x = 0.675$; $y = 0.324$). The results of PL and PLE spectra indicate the applicability of $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}$ as a red component in lamp phosphor. The phosphor is characterized through XRD pattern analysis, and morphology is explained on the basis of SEM image. Optimum concentration of Eu^{3+} required for the highest intensity of emission is also studied.

1. Introduction

Borates as host for light emitting materials under UV excitation have attracted much attention. The reason behind their being in a focus of research is their variety of structure types, transparency to a wide range of wavelengths, and high optical quality [1–4]. Also borates possess excellent properties as host due to the inherent attributes of the large band gap and covalent bond energy. A variety of borate host materials doped with rare earth and other ions have been studied and reported [5]. Moreover, B–O bond generally has no absorption in near UV region and has absorption in deep UV region because of its large covalent bond energy. Some previous works show that Eu^{3+} doped borates exhibit relatively strong absorption in the UV region and intense red emission with good color purity [6, 7].

Recently the alkali earth metal (M) yttrium borates ($\text{M}_2\text{Y}_2\text{B}_2\text{O}_7$) have been well known hosts for luminescent material with better crystallinity, lower synthesis temperature, and higher radiation efficiency, as compared to the corresponding simple alkali earth metal borates [8]. The $\text{Na}_2\text{Y}_2\text{B}_2\text{O}_7$ is an excellent host for luminescent materials which supports all the possible trivalent rare earth dopants and shows intense emission from violet region to red region [9]. In the present work, we investigate, for the first time, the photoluminescence characteristics of Eu^{3+} doped $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7$.

The purpose of replacing the mostly studied Na^+ by K^+ is to find the ion type dependence of Eu^{3+} luminescence in $\text{M}_2\text{Y}_2\text{B}_2\text{O}_7$ host. The photoluminescence properties of the synthesized materials were studied using a fluorescence spectrometer (Hitachi F-7000).

2. Experimental

2.1. Sample Preparation. The powder samples of the phosphor $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7$ with different concentrations of Eu^{3+} (0.001, 0.002, 0.005, 0.01, and 0.02) have been prepared by solution combustion technique. The method is based on the exothermic reaction between the fuel (urea) and oxidizer (ammonium nitrate). The detailed description of the method regarding the measurement of stoichiometric quantities of fuel and oxidizer is reported in our earlier work [10–13].

All the ingredients, yttrium nitrate ($\text{Y}(\text{NO}_3)_3$), boric acid (H_3BO_3), potassium nitrate (KNO_3), urea ($\text{NH}_2\text{—CO—NH}_2$), and ammonium nitrate (NH_4NO_3) used, are of AR grade and the rare earth Eu_2O_3 (99.99% purity) used is from the Indian Rare Earths. The stoichiometric amounts of the ingredients are thoroughly mixed in an agate mortar. Later, little amount of double distilled water was added to get an aqueous homogeneous solution. The solution is then transferred into a China Basin and slowly heated at

lower temperature at 90°C in order to remove the excess of water contents. The thick paste obtained after heating is then transferred into a preheated muffle furnace maintained at $(550 \pm 10)^\circ\text{C}$. The paste boils foams and ignites to burn with flame; lastly, a voluminous, foamy powder is obtained. This entire combustion process is over in about 5 min. Following the combustion, the resulting fine powders were annealed in slightly reducing atmosphere (produced by burning charcoal) at a temperature of 750°C for about 60 min and suddenly cooled to room temperature [14]. The same process of synthesis is repeated for different concentrations of activator.

2.2. Characterization Techniques. $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ materials were characterized by using Rigaku Miniflex II X-ray diffractometer with scan speed of 2.000°/min and with Cu K α radiation. SEM images are produced on Philips XL 30 SEM system having a resolution of 2.0 nm at 30 kV and 0.5 nm at 1 kV. The PL and PLE spectra are recorded on Hitachi F-7000 fluorescence spectrometer by keeping slit window at 1.0 nm for excitation and emission and PMT voltage at 400 V.

3. Results and Discussion

3.1. XRD Pattern for $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7$. The studies on novel yttrium based borate phosphor become a hot issue in exploring new phosphor materials, which have also been proved to be efficient in the application of light conversion. $\text{Na}_2\text{Y}_2\text{B}_2\text{O}_7$ phosphor was first reported by Zhang and Li [15] as a near-UV white LEDs phosphor prepared by high temperature solid state synthesis method. The material was described in the monoclinic crystal system. In this paper it has been decided to replace sodium by potassium (having the same valence) to get $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7$.

The X-ray diffraction patterns of $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7$ with different concentrations of activator Eu^{3+} are shown in Figure 1 to verify the phase purity and crystal similarity. All the peaks in different patterns are in good agreement with each other, which indicates that all the prepared samples are in a similar phase, and the increasing concentration of dopants does not affect the crystal structure. However, the obtained diffraction peaks of compound are in some agreement with the two different phases in the ICDD database, namely, $\text{Y}_2\text{B}_2\text{O}_6$ (~80%) and K_2O (~20%). Having in mind that the quantities of the starting materials are chosen according to the given chemical composition of $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ matrix, therefore (even if in a mixed phase) this was named as $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ phosphor in this paper [16].

The results also imply that the prepared samples are not the simple physical mixtures of precursor used but may be a new single-host $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7$ material. The detailed studies on structures of these materials are still under investigation. Therefore, only XRD data of $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7$ is reported in this paper.

3.2. Surface Morphology of $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$. The SEM photographs of $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ phosphor clearly show that the grains are irregular in shape and have a size less than 1 μm . The typical morphological images are represented in Figure 2.

FIGURE 1: XRD patterns for $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7$ doped with different concentrations of Eu.

FIGURE 2: Representative SEM image for $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7$.

The particles possess foamy like morphology formed from highly agglomerated crystallites. An average crystallite size is in submicrometer range of $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ phosphors.

3.3. Luminescence Properties of Eu^{3+} Activated $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7$. Figure 3 represents excitation and emission behaviors of Eu^{3+} activated $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7$ prepared at 750°C. The excitation spectra exhibit a broad band centered at 260 nm related to the charge transfer (CT) from the 2p orbital of the O^{2-} ions to the 4f orbital of Eu^{3+} ions [17]. Other minor peaks, 300–400 nm, are associated with the direct excitation of electrons for the f-f shell transitions in Eu^{3+} ions.

The emission spectra of Eu doped $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7$ under the charge transfer (CT) band excitation at 260 nm essentially contain groups of lines between 500 and 650 nm. The lines in the 500–550 nm range (shown in Figure 3 (inset)) are attributed to $^5\text{D}_1$ to $^7\text{F}_j$ transition of Eu^{3+} and are found to be very weak. The lines in the 550–650 nm range correspond to transitions from the first excited state $^5\text{D}_0$ to the $^7\text{F}_j$ levels ($J = 0-3$). It is well known that the relative intensity of the $^5\text{D}_0$ - $^7\text{F}_1$ and $^5\text{D}_0$ - $^7\text{F}_2$ transitions strongly depends on the local symmetry of the Eu^{3+} ions. When the Eu^{3+} ions occupy sites with inversion centers, the $^5\text{D}_0$ - $^7\text{F}_1$ (the magnetic dipole) transition should be relatively strong, while the $^5\text{D}_0$ - $^7\text{F}_2$ (the electric dipole) transition is parity-forbidden and should be very weak. The emission spectra of the compound $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7$ exhibit strong red luminescence of $^5\text{D}_0$ - $^7\text{F}_2$ at 613 nm indicating that the Eu^{3+} ion is located in a noncentrosymmetric

FIGURE 3: Excitation and emission spectra for $K_2Y_2B_2O_7$ doped with 0.01 mole of Eu.

position in the matrix. For Eu^{3+} doped $Na_2Y_2B_2O_7$, after the Eu^{3+} ions have entered the crystal lattice, they will occupy Y sites and Y ions indeed occupy very low symmetry sites, C_1 . According to group theory selection rules, the magnetic dipole and the electric dipole are permitted and the electric dipole transition is the stronger one [18]. Taking the same reference in account it may be suggested that in Eu^{3+} doped $K_2Y_2B_2O_7$ phosphor Eu^{3+} also takes the same low symmetry site.

3.4. Concentration Quenching Effect. Generally speaking, the doping concentration has a significant effect on the phosphor performance. The effect of Eu^{3+} doping concentration (x) in the $K_2Y_2B_2O_7:xEu^{3+}$ ($x = 0.001, 0.002, 0.005, 0.01$, and 0.02) phosphors on the relative intensity of the electronic dipole transition ($^5D_0-^7F_2$) is shown in Figure 4. The result shows that, as the concentration of Eu^{3+} increases, the luminescent intensity also increases and reaches the highest intensity when the doping concentration of Eu^{3+} increases to 0.01. However, the luminescent intensity slightly decreases as long as the concentration is over 0.01 due to concentration quenching. The energy transfer within the same rare earth ions results in the concentration quenching associated with the exchange interaction [5].

The concentration quenching phenomenon can be theoretically supported by the relationship between luminescent intensity I and doping concentration x mathematically expressed as

$$I \propto \alpha^{(1-s/d)} \Gamma\left(1 + \frac{s}{d}\right), \quad (1)$$

$$\alpha = x\Gamma\left(1 - \frac{s}{d}\right) \left[X_0\left(\alpha + \frac{A}{\gamma}\right)\right]^{d/s},$$

where γ is the intrinsic transition probability of the sensitizer and s is the index of electric multipole, for electric dipole-electric dipole, electric dipole-electric quadrupole, and electric quadrupole-electric quadrupole corresponding to 6, 8,

FIGURE 4: Peak intensity versus concentration of Eu in $K_2Y_2B_2O_7$ ($\lambda_{ex} = 260$ nm).

FIGURE 5: The relation of the concentration of Eu^{3+} ions $\log(x)$ and $\log(I/x)$ for the $^5D_0 \rightarrow ^7F_2$ transition in the $K_2Y_2B_2O_7$ phosphor.

and 10, respectively. d denotes a dimension of the sample, and here $d = 3$ owing to the energy transfer between Eu^{3+} inside the grains. A and X_0 are constants, and $\Gamma(1 + s/d)$ is a Γ function. From (1), it can be obtained that

$$\log\left(\frac{I}{x}\right) = -\frac{s}{d} \log(x) + \log f, \quad (2)$$

where f is independent of the doping concentration. Figure 5 presents the $\log(I/x) - \log(x)$ plots for the $^5D_0-^7F_2$ transition of Eu^{3+} in the $K_2Y_2B_2O_7$ host. According to (2), the value of the slope parameter $-(s/d)$ is calculated to be -0.89 (close to -1) corresponding to $s = 3$ by linear approximation idea [19]. This suggests that the exchange interaction mechanism plays a central role in the energy transfer among Eu^{3+} ions in the phosphors $K_2Y_2B_2O_7$.

FIGURE 6: CIE coordinate for 613 nm emission of $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$.

3.5. CIE Diagram. The CIE 1931 color space chromaticity diagram to illustrate the chromaticity of $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ phosphors. Figure 6 represents that the CIE coordinates of $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ were measured as ($x = 0.675$; $y = 0.324$). The location of coordinate has been marked in Figure 3 with a green circle. The CIE coordinates of $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ are in the bright red area.

4. Conclusion

For $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7$ doped with europium, the XRD pattern shows that the material was highly crystalline, having multiple peaks related to precursor or dopants, and the SEM image indicates the crystalline nature of this phosphor, with agglomerated regular morphology. Photoluminescence properties show that the phosphor gives strong red emission (PL) at 613 nm related to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} under the 260 nm excitation (PLE) related to the charge transfer (CT) from the 2p orbital of the O^{2-} ions to the 4f orbital of Eu^{3+} ions with CIE coordinates ($x = 0.675$; $y = 0.324$). The results of PL and PLE spectra indicate the applicability of $\text{K}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ as a red component in lamp phosphor.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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