

Effect of Eu^{3+} doping on fluorescence properties of novel phosphor $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$

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The novel europium doped $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$ red phosphors have been prepared by a combustion synthesis. The structure and morphology of the $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ were investigated using X-Ray diffraction (XRD) pattern and scanning electron microscopy (SEM) respectively. Photoluminescence (PL) properties of as-prepared phosphors were investigated on fluorescence spectrometer (F-7000). $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ synthesized phosphor shows CIE color coordinates of with good red intensity. Optimum concentration of Eu^{3+} required for the highest intensity of emission is also studied.

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1. Introduction

Borate based phosphors are attracted much attention for their uses in many applications in the field of luminescence. Borate is a key compound for most of the phosphors, which is studied for various applications. Borate based host have been a focus of research for their variety of structure types, transparency to a wide range of wavelengths and high optical quality [1, 2]. The outstanding properties of borate host possess structure of phosphor because of inherent attributes of the large band gap and covalent bond energy. Moreover, B–O bond generally has no absorption in shallow UV region and has absorption in deep UV region because of its large covalent bond energy. Now a day, variety of borate based phosphors doped with rare earth and other ions have been reported for a variety of applications [3] such as inorganic borate host compounds doped with rare earth ions are the important class of phosphors useful for LED based solid state light [4]. Also Eu^{3+} ions is an excellent activator have been widely used in red-emitting phosphors [5] and previous work on luminescence in borate phosphor show that Eu^{3+} -doped borates exhibit relatively strong absorption in the UV region and intense red emission with good color purity [6].

Also, recently the alkali earth metal (M=Li, Na and K) yttrium borates based phosphor ($\text{M}_2\text{Y}_2\text{B}_2\text{O}_7$) have been well known hosts for luminescence materials with better crystallinity, lower synthesis temperature and higher radiant efficiency, as compared to the corresponding borates [7]. 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 dopant and shows intense emission from violet region to red region [8].

Inspiring from above discussion on borates and yttrium borate based materials. In the present work, we first time investigate the photoluminescence characteristics of Eu^{3+} doped $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$. The purpose of replacing Li^+ by most studied K^+/Na^+ to find out the ion dependence of Eu^{3+} luminescence in $\text{M}_2\text{Y}_2\text{B}_2\text{O}_7$ host.

2. Experimental

The novel phosphor $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ (0.001, 0.002, 0.005, 0.01, and 0.02) has been prepared by a combustion technique. The detailed description of the method was reported in our earlier work [9-11]. All the ingredients yttrium nitrite $\text{Y}(\text{NO}_3)_3$, boric acid H_3BO_3 , lithium nitrite $\text{Li}(\text{NO}_3)$, urea $\text{NH}_2\text{-CO-NH}_2$ and ammonium nitrite NH_4NO_3 were used (AR grade) and the rare earth Eu_2O_3 (99.99% purity) were used from the Indian rare earth. The stoichiometric amounts of ingredients were thoroughly mixed in an agate mortar, then adding little amount of double distilled water to get an aqueous homogeneous solution. This solution was then transferred into a china basin and slowly heated at lower temperature of 90°C in order to remove the excess water. The solution was then again transferred into a preheated muffle furnace maintained at $(550 \pm 10)^\circ\text{C}$. The solution boils foams and ignites to burns with flame; a voluminous, foamy powder was obtained. This entire combustion process was over in about 5 min [12]. The molar ratio and weights of the ingredients used were shown in the Table 1. Following the combustion, the resulting fine powders were annealed at temperature 750°C for 1h and quenched to room temperature. The samples are subjected to XRD analysis. PL measurements were performed on fluorescence spectrometer (Hitachi F-7000).

Table 1. Molar ratio and weights of the ingredients for $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$.

Molar Ratio of the Constituents	$\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$
$\text{Li}(\text{NO}_3)$	2
$2\text{Y}(\text{NO}_3)_3 + \text{xEu}_2\text{O}_3$	$2-\text{x}(0.001-0.02)$
H_3BO_3	2
$\text{CO}(\text{NH}_2)_2$	8
NH_4NO_3	4

3. Results and discussion

3.1. XRD phase analysis

The XRD pattern of Eu^{3+} ion doped $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$ phosphors were analyze structure confirmation of as-synthesized phosphors. $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$ doped with Eu^{3+} is first time prepared and analyzed careful for peak to peak comparison with the available ICDD database; it is found that there is no standard ICDD file available to match the structure of this phosphor. Also pattern did not indicate the presence of phases or peaks from precursor material like $\text{Y}(\text{NO}_3)_3$, $\text{Li}(\text{NO}_3)_3$, H_3BO_3 , and other likely phases (i.e. LiYO_2 , Y_2O_3 , $\text{Li}_2\text{B}_4\text{O}_7$, YBO_3). So according to the stoichiometric balance calculated using chemical composition of $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$, we interpreted that the final product was formed in crystalline and homogeneous form called to be $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$. This results may indicate that the prepared samples are not the simple chemical mixtures of $\text{Y}(\text{NO}_3)_3$ (2 mol), $\text{Li}(\text{NO}_3)_3$ (1 mol), H_3BO_3 (2 mol) but a new novel host $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$ material. Therefore it is indirect evidence for the complete formation and conformation of $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$ compound [13]. Therefore Fig. 1 show that it might be inferred that our compound has formed in the present phase and there was no effect of Eu^{3+} concentration on XRD pattern. The detailed studies on structures of these materials are still under investigation. Therefore, only XRD data of $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$ is reported in this paper.

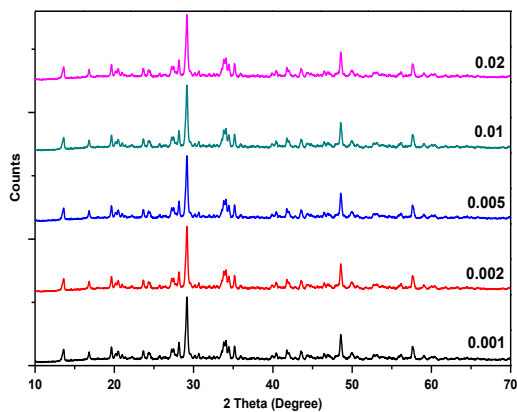


Fig. 1. XRD pattern of $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$ doped with various concentration of Eu^{3+} .

3.2. Surface morphology of $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$

The SEM photographs of $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ phosphor clearly show that the grains are irregular in shape and have a size less than $1\ \mu\text{m}$. The typical morphological images are represented in Fig. 2. Average crystallite size was in sub micrometer range of $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ phosphors.

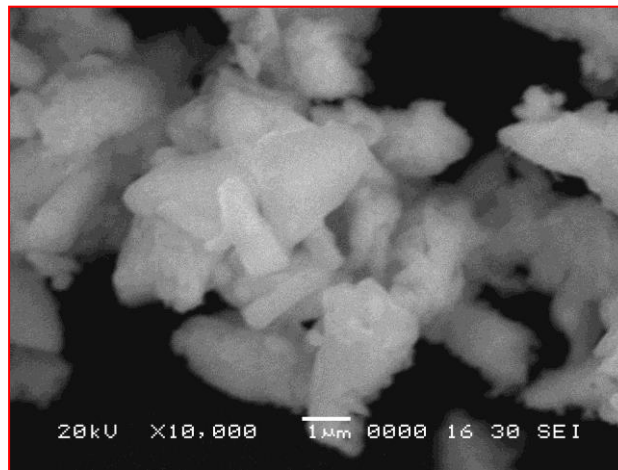


Fig. 2. Representative SEM image of $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$.

3.3. Photoluminescence properties of $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$

Fig. 3 show photoluminescence spectra of $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$. The excitation spectra of $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ consists of broaden band at 234 nm, which correspond to the $\text{F}\rightarrow\text{D}$ transitions of Eu^{3+} and the phosphor show most intense emission of located at 613 nm (corresponding to ${}^5\text{D}_0\rightarrow{}^7\text{F}_1$) followed by a weak shoulders in region 550-600 nm (${}^5\text{D}_0\rightarrow{}^7\text{F}_{j(j=0,1)}$) under 234 nm excitation. It is well known that the relative intensity of the ${}^5\text{D}_0\rightarrow{}^7\text{F}_1$ and ${}^5\text{D}_0\rightarrow{}^7\text{F}_2$ transitions strongly depends on the local symmetry of the Eu^{3+} ions. The relative intensity due to magnetic dipole transition Eu^{3+} ions occupy sites with inversion centers of ${}^5\text{D}_0\rightarrow{}^7\text{F}_1$ and the electric dipole transition is parity-forbidden and be supposed to be weak ${}^5\text{D}_0\rightarrow{}^7\text{F}_2$ which are depended strongly on the symmetry of the crystal lattice around Eu^{3+} [14]. It is clearly observed from the results that in host $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$ the electric dipole transition from Eu^{3+} are stronger than magnetic transitions.

The comparison of results with the most reported phosphor $\text{Na}_2\text{Y}_2\text{B}_2\text{O}_7$ shows that Eu^{3+} gives the same emission in $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$. Thus the material can be utilized in the place of $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$. The result also confirm the formation of material as both $\text{Na}_2\text{Y}_2\text{B}_2\text{O}_7$ and $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$ are from the same family and gives same excitation and emission for dopant Eu^{3+} .

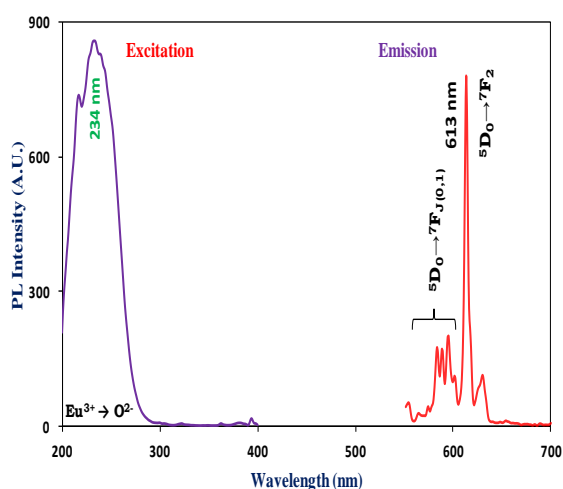


Fig. 3. Combine excitation and emission spectra for $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$ activated with Eu^{3+} .

Effect of Eu^{3+} doping concentration (x) in the $\text{Li}_2\text{Y}_{(2-x)}\text{B}_2\text{O}_7:\text{Eu}^{3+}$ ($x = 0.001, 0.002, 0.005, 0.01,$ and 0.02) phosphors on the relative intensity of the electronic dipole transition (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$) is shown in Fig. 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.

Fig. 5 represents the CIE 1931 color space chromaticity diagram to illustrate the chromaticity of $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ phosphors. CIE coordinates for all concentration of Eu^{3+} doped $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$ phosphor measured to be ($x = 0.675, y = 0.324$). The location of coordinate has been marked in Fig. 5 with a green circle. The CIE coordinates of $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ are in the bright red area.

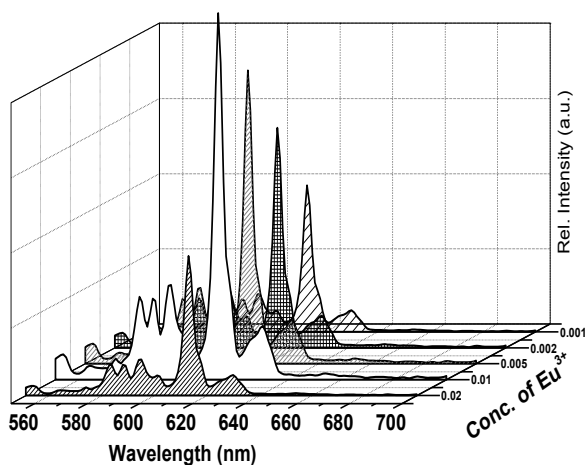


Fig. 4. Emission Spectra of $\text{Li}_2\text{Y}_{(2-x)}\text{B}_2\text{O}_7:\text{Eu}^{3+}$ ($x = 0.001, 0.002, 0.005, 0.01,$ and 0.02) phosphors.

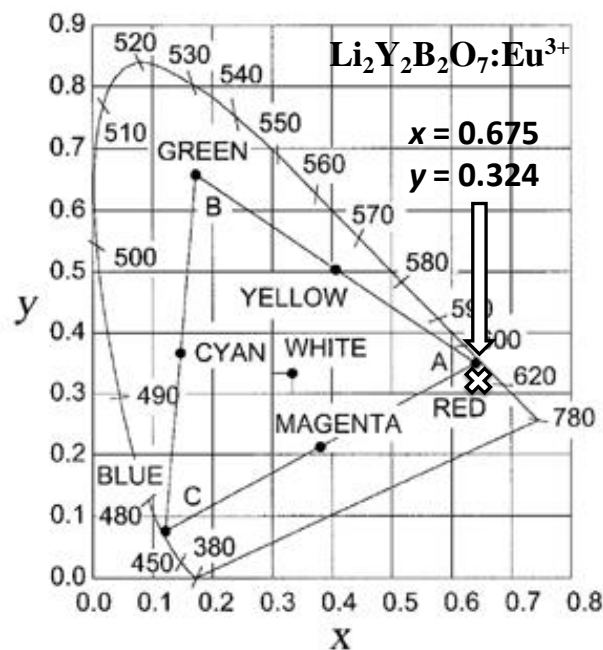


Fig. 5. CIE color space chromaticity diagram of $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ phosphor.

4. Conclusion

$\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7:\text{Eu}^{3+}$ phosphors were successfully prepared by combustion synthesis. The XRD pattern of $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$ not reported yet by any method. The SEM image indicates the crystalline nature of this phosphor, with agglomerated regular morphology. PL properties show phosphors gives strong red emission at 613 nm corresponding to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition of Eu^{3+} ion monitored at 234 nm excitation. PL spectra of $\text{Li}_2\text{Y}_2\text{B}_2\text{O}_7$ crystalline material annealed at room temperatures with various concentration of Eu^{3+} and The CIE coordinates of the synthesized sample was (0.675, 0.324).

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