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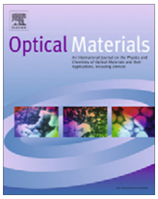

A red-emitting heavy doped phosphor $Li_6Y(BO_3)_3:Eu^{3+}$ for white light-emitting diodes

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ABSTRACT

A series of Eu^{3+} activated $Li_6Y_{1-x}Eu_x(BO_3)_3$ ($0.05 \leqslant x \leqslant 1$) phosphors were synthesized by solid-state reaction method. The structures and photoluminescent properties of the phosphors were investigated at room temperature. The results of XRD patterns indicate that these phosphors are isotypic to the monoclinic $Li_6Gd(BO_3)_3$. The excitation spectra indicate that these phosphors can be effectively excited by near UV (370–410 nm) light. The red emission from transition $^5D_0 \rightarrow {}^7F_2$ is dominant. The emission spectra exhibit strong red performance (CIE chromaticity coordinates: $x = 0.65$, $y = 0.35$), which is due to the $^5D_0 - {}^7F_J$ transitions of Eu^{3+} ions. The relationship between the structure and the photoluminescent properties of the phosphors was studied. The concentration quenching occurs at $x \approx 0.85$ under near UV excitation. $Li_6Y(BO_3)_3:Eu^{3+}$ has potential application as a phosphor for white light-emitting diodes.

1. Introduction

In the last few years, UV LED based phosphor-converted white LEDs (pc-WLED) have attracted great attention [1–29]. Since the current commercially available red phosphor $Y_2O_2S:Eu^{3+}$ is chemically unstable under UV radiation [1,3,8,14–18,22,25,27], Eu^{3+} doped red phosphors focused on matrixes with high valence transition metal groups are extensively studied, such as $CaMO_4:Eu^{3+}$ [8], $CaWO_4:Eu^{3+}$ [9], $Ca_3(VO_4)_2:Eu^{3+}$, Sm^{3+} [10], $NaEu_{1-x}Sm_x(MoO_4)_2$ [11], $LiEu_{1-x}Bi_x(MoO_4)_2$ [12], $Y_2W_{1-x}Mo_xO_6:Eu^{3+}$, Bi^{3+} [13], $Na_5Eu(MoO_4)_4$ [14,15], $BaGd_{2-x}Eu_x(MoO_4)_4$ [16], $(Y,Gd)VO_4:Eu^{3+}$, Sm^{3+}, Bi^{3+}[17], and [18–21]. There are also some phosphors without high valence transition metal groups [22–29]. For the phosphor used in pc-WLEDs, strong broad absorption bands in the UV region 370–400 nm are required to match the VU LED emission band [1,30,31]. However, all of the phosphors reported in Refs. [8–28] have narrow line-shaped excitation peaks at near UV (370–410 nm), which are not desirable for pc-WLEDs. The charge-transfer band (CTB) edges of O–Eu/O–W/O–Mo/O–V in these compounds usually appear at short wavelength (<350 nm), although these materials normally perform effective red emission. The absorption edges of CTB in some Eu^{3+} doped perovskite type molybdates, such as $(Ba,Sr)_2CaMoO_6$ [32–34], locate at relatively low energy (~450 nm). However, high efficiency is not expected in these materials, because the luminescence efficiency of phosphors doped Eu^{3+} ions decreases with energy decreasing of CTB [35]. Therefore, the CTB absorption is not an option for Eu^{3+} activated phosphors used in pc-WLEDs.

The energy levels $^5L_{6,7}$,^5G_J of Eu^{3+} are very close to each other [36], they actually form a broad band at 370–410 nm in solids. However, the oscillator strength of $^7F_0 \rightarrow {}^5L_7$,$^5G_J$ is much lower than $^7F_0 \rightarrow {}^5L_6$ in matrixes with high valence transition metal groups [8–21]. Our research group recently focused on Eu^{3+} activated borate red phosphors, since they may have strong absorption bands at 370–410 nm ($^7F_0 \rightarrow {}^5L_{6,7}$,$^5G_J$).

$Li_6R(BO_3)_3$ (R = trivalent rare earth ions) are attractive matrix materials owing to their high transparency in the UV and high damage threshold for exposure to energetic radiations [37]. The polycrystalline $Li_6R(BO_3)_3$ belongs to the monoclinic system with space group $P2_1/c$ (Number = 14, $Z = 4$) [38,39]. $Li_6R(BO_3)_3$ have been intensively studied as thermoluminescent materials [40], laser medium [37,41] or photoluminescent materials [39,42–45]. However, there are no detailed reports on the photoluminescent properties of $Li_6R(BO_3)_3:Eu^{3+}$ under near UV excitation, i.e. little research on potential application in pc-WLEDs has been report. The main purpose of this work is to directly investigate the spectroscopic properties of $Li_6R(BO_3)_3:Eu^{3+}$ under near UV excitation and possible applications.

2. Experimental

2.1. Synthesis

The powder samples of $Li_6Y_{1-x}Eu_x(BO_3)_3$ ($0.05 \leqslant x \leqslant 1$) were prepared by solid-state reaction technique at high temperature.

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The starting materials were Li_2CO_3 (A.R.), H_3BO_3 (A.R.), Y_2O_3 (4N) and Eu_2O_3 (4N). All raw materials with stoichiometric amounts were mixed homogeneously in an agate mortar. The homogeneous mixture was put into a corundum crucible and sintered at 800 °C in air for 5 h. Finally, the samples were cooled to room temperature in the furnace, and ground again into powder for subsequent characterizations.

2.2. Measurement

The phase purity of the prepared phosphors was investigated by an X-ray diffractometer with Cu Kα radiation (wavelength = 0.15406 nm) at 36 kV tube voltage and 20 mA tube current. The excitation, emission spectra and decay curves of all the samples were measured by a Hitachi F-7000 Fluorescence Spectrophotometer at room temperature.

3. Results and discussion

3.1. XRD phase analysis

The X-ray powder diffraction (XRD) patterns of $Li_6Y_{1-x}Eu_x(BO_3)_3$ were measured. As examples, the patterns of the phosphors for $x = 0.05$ and 0.85 are shown in Fig. 1. The results of XRD analysis confirm that the compounds were obtained as single phase. No extra peak related to the starting materials was observed. All the pattern curves are very similar to each other and very consistent with the PDF#54-1119 ($Li_6Gd(BO_3)_3$). The results indicate that these phosphors are isotypic to the monoclinic $Li_6Gd(BO_3)_3$. There is no detectable phase change within the whole range of Eu^{3+} concentration. The radius of Eu^{3+} ion (~106.6 pm) is almost equal to that of Y^{3+} ion (~101.9 pm) with coordination number eight [46]; therefore, Eu^{3+} and Y^{3+} can form a continuous solid solution in the matrix. These prepared samples crystallize as monoclinic system with space group $P2_1/c$, and the lattice parameters of $Li_6Y_{0.15}Eu_{0.85}(BO_3)_3$ were calculated as follows: $a = 0.7236$ nm, $b = 1.6584$ nm, $c = 0.6693$ nm and $\beta = 105.42°$. The site symmetry of R^{3+} is C_1 [42–44]. The rare-earth ions are surrounded by eight oxygen ions. The RO_8 polyhedra connect each other by common edges to form infinite zigzag chains parallel to the c axis. The intrachain and interchain distances of R–R are about 0.39 nm and 0.66 nm respectively [38,39].

3.2. Photoluminescent properties of $Li_6Y_{1-x}Eu_x(BO_3)_3$

The phosphors $Li_6Y_{1-x}Eu_x(BO_3)_3$ with different doping concentration of Eu^{3+} show similar excitation and emission spectra except for their intensities. Different monitor/excitation wavelengths do not change the shape and position of spectra either. The relative excitation spectrum of $Li_6Y_{0.15}Eu_{0.85}(BO_3)_3$ by monitoring $^5D_0 \rightarrow {}^7F_2$ ($\lambda_{em} = 614$ nm) emission is shown in Fig. 2. It can be seen clearly that the excitation spectrum consists of a broad band and a group of sharp peaks in the visible and UV region. The broad excitation band centered at ~265 nm can be attributed to the CTB transition arising from O^{2-} ion to Eu^{3+} ion, which suggests that the phosphor is a possible candidate for fluorescent lamps to substitute costly $Y_2O_3:Eu^{3+}$. The sharp peaks are ascribed to the intra-configurational 4f–4f transitions of Eu^{3+} in the matrix: $^7F_0$ to $^5F_4$, $^5H_6$, $^5H_3$, $^5D_4$, (^5G_J and $^5L_7$ manifold), $^5L_6$, $^5D_3$, $^5D_2$, $^5D_1$ and $^7F_1$ to $^5D_1$ at wavelengths 298, 318, 326, 361, 378, 393, 417, 464, 525 and 536 nm, respectively [36]. The strongest excitation bands in the near UV region are at 370–410 nm ($^7F_0 \rightarrow {}^5L_{6,7}, {}^5G_J$) and its full width at half maximum (FWHM) is about 22 nm, which matches the emission wavelengths of near UV LED chips.

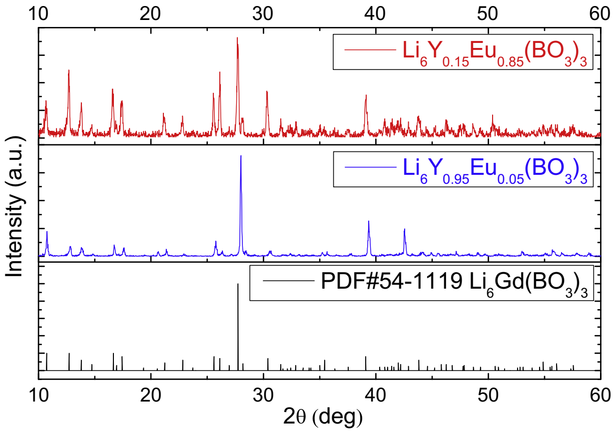

Fig. 1. The XRD patterns of the samples.

The Eu^{3+} activated compounds $Li_6Y_{1-x}Eu_x(BO_3)_3$ show strong red emission under 393 nm excitation. The relative emission spectrum of $Li_6Y_{0.15}Eu_{0.85}(BO_3)_3$ under 393 nm excitation is given in Fig. 3. The emission spectrum is composed of groups of sharp peaks from the emission of Eu^{3+} intra-configurational 4f–4f transitions ($^5D_0 \rightarrow {}^7F_{0-4}$) at 581, 595, 614, 649 and 707 nm, respectively. No emission peaks arising from level higher than $^5D_0$, even for low concentration of Eu^{3+}, because of efficient multi-phonon relaxation

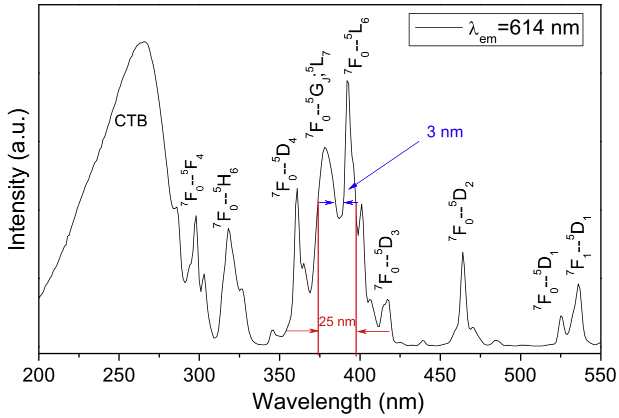

Fig. 2. The excitation spectrum of $Li_6Y_{0.15}Eu_{0.85}(BO_3)_3$.

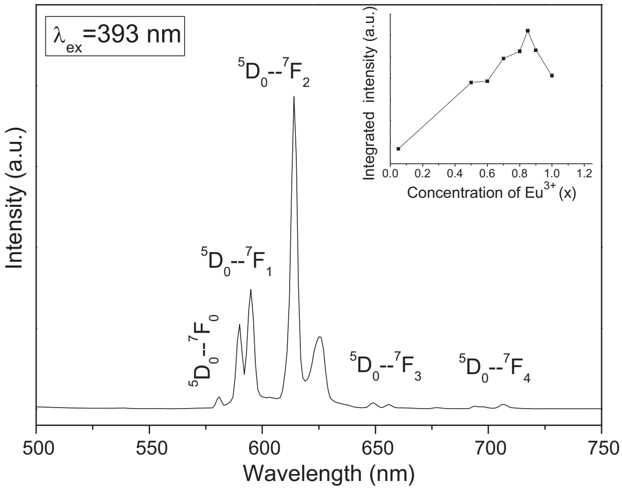

Fig. 3. The emission spectrum of $Li_6Y_{0.15}Eu_{0.85}(BO_3)_3$. Inset: Integrated emission intensity of $Li_6Y_{1-x}Eu_x(BO_3)_3$ depends on the concentration (x) of Eu^{3+}.