

# Luminescence properties of $\text{LiY}_6\text{O}_5(\text{BO}_3)_3:\text{Eu}^{3+}/\text{Sm}^{3+}$ phosphor



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## ABSTRACT

$\text{Eu}^{3+}$ ,  $\text{Sm}^{3+}$  single-doped and co-doped  $\text{LiY}_6\text{O}_5(\text{BO}_3)_3$  phosphors are prepared by a high-temperature solid-state reaction method. The  $\text{Eu}^{3+}$ -doped and  $\text{Sm}^{3+}$ -doped phosphors give bright red emission centered at 613 and 604 nm under 395- and 406-nm excitation, respectively, while the  $\text{Eu}^{3+}$ ,  $\text{Sm}^{3+}$  co-doped phosphor just gives  $\text{Eu}^{3+}$ -characterized emission whether excited by 395 or 406 nm. This indicates that the co-doped  $\text{Sm}^{3+}$  ions can broaden the excitation band of the phosphor without changing its color index, which might match better with the near-ultraviolet (NUV) chips in white light-emitting diode (W-LED) application. The  $\text{Sm}^{3+}$ -concentration-dependent luminescence properties ascribed to the energy transfer between  $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$  is discussed.

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## 1. Introduction

At present, research on white light-emitting diodes (W-LEDs) has become an active field for constant attention to energy saving [1–3]. According to the statistics, the energy consumption of the W-LEDs only accounts for 20% of incandescent lamps and 50% of fluorescent lamps. Moreover, the W-LEDs have other advantages including high brightness, long lifetime, and environmental protection [4,5]. W-LEDs are believed to be one of the next-generation light-emitting devices, which may replace the existing general lightings [1–6]. Presently, the method of generating W-LEDs usually combines a blue light-emitting chip with a yellow-emitting phosphor such as  $\text{Ce}^{3+}$ -doped yttrium aluminum garnet (YAG: $\text{Ce}^{3+}$ ) [7,8]. However, this kind of W-LEDs shows a relatively low color rendering index and high color temperature due to the absence of a long-wavelength red component in the visible spectrum [7,9]. Thanks to significant research progress on ultraviolet (UV)-LEDs, the abovementioned problem might be solved by fabricating W-LEDs with a near-ultraviolet (NUV) chip plus blue, green, and red (RGB) tricolor phosphors. Therefore, it is an urgent task to search for efficient LED phosphors excited by NUV light [8]. Yet the red light-emitting phosphors for W-LEDs based on an NUV chip are still limited to the unstable sulfide-based materials, which shorten the lifetime of W-LEDs. Thus, it is necessary to develop a red phosphor with excellent chemical stability under NUV light excitation.

Borates have been extensively investigated as host lattices for luminescent materials. Some borate phosphors, such as  $(\text{Y}, \text{Gd})\text{BO}_3:\text{Eu}$ ,  $\text{SrB}_4\text{O}_7:\text{Eu}$ ,  $\text{Tb}$ , and  $\text{GdAl}_3(\text{BO}_3)_4:\text{Eu}$  [10–12], exhibit high luminescence efficiency, good chemical stability, and low preparation temperature. More interestingly, a recent investigation shows that  $\text{Eu}^{3+}$  ions doped into  $\text{ZnB}_2\text{O}_4$  can strongly absorb NUV light in the range of 380–400 nm and gives red emission at 610 nm with high quantum efficiency. This indicates that a suitable borate host doped with  $\text{Eu}^{3+}$  can be used for creating efficient red phosphors for NUV LED application.

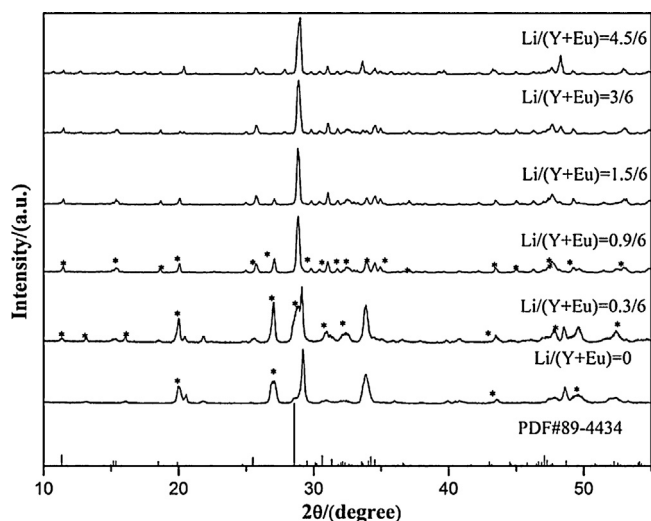
The new family of lithium rare earth oxyborates of formula  $\text{LiLn}_6\text{O}_5(\text{BO}_3)_3$  ( $\text{Ln} = \text{Pr} - \text{Tm}$  and  $\text{Y}$ ) was first discovered by Chaminate et al. [13] in the ternary-phase diagrams  $\text{Li}_2\text{O}-\text{Ln}_2\text{O}_3-\text{B}_2\text{O}_3$ . In 2003, the luminescence characteristics of  $\text{Eu}^{3+}$  in the  $\text{LiLn}_6\text{O}_5(\text{BO}_3)_3$  host ( $\text{Ln} = \text{Y}, \text{Gd}$ ) [14] were preliminarily studied under UV excitation. The phosphor presents excellent red emission at 613 nm under 248-nm excitation.

In order to further explore the luminescence properties of rare earth-doped  $\text{LiY}_6\text{O}_5(\text{BO}_3)_3$  under NUV (380–410-nm) excitation,  $\text{Eu}^{3+}$ ,  $\text{Sm}^{3+}$  single-doped and co-doped  $\text{LiY}_6\text{O}_5(\text{BO}_3)_3$  phosphors have been prepared in this work. Excess of  $\text{Li}_2\text{CO}_3$  was introduced to promote the formation of  $\text{LiY}_6\text{O}_5(\text{BO}_3)_3$  powder. The doping concentration-dependent luminescence properties and the energy transfer mechanism between  $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$  ions have been investigated in these phosphors.

## 2. Experimental

$\text{LiY}_6\text{O}_5(\text{BO}_3)_3:\text{M}^{3+}$  ( $\text{M} = \text{Eu}, \text{Sm}$ ) phosphors were synthesized by a high-temperature solid-state reaction.  $\text{Li}_2\text{CO}_3$  (A.R.),  $\text{H}_3\text{BO}_3$

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**Fig. 1.** XRD patterns of  $\text{Li}_g\text{Y}_{4.2}\text{O}_5(\text{BO}_3)_3:0.3\text{Eu}^{3+}$  ( $g=0, 0.3, 0.9, 1.5, 3,$  and  $4.5$ ); the peaks marked by asterisks are from  $\text{Y}_2\text{O}_3$  impurity.

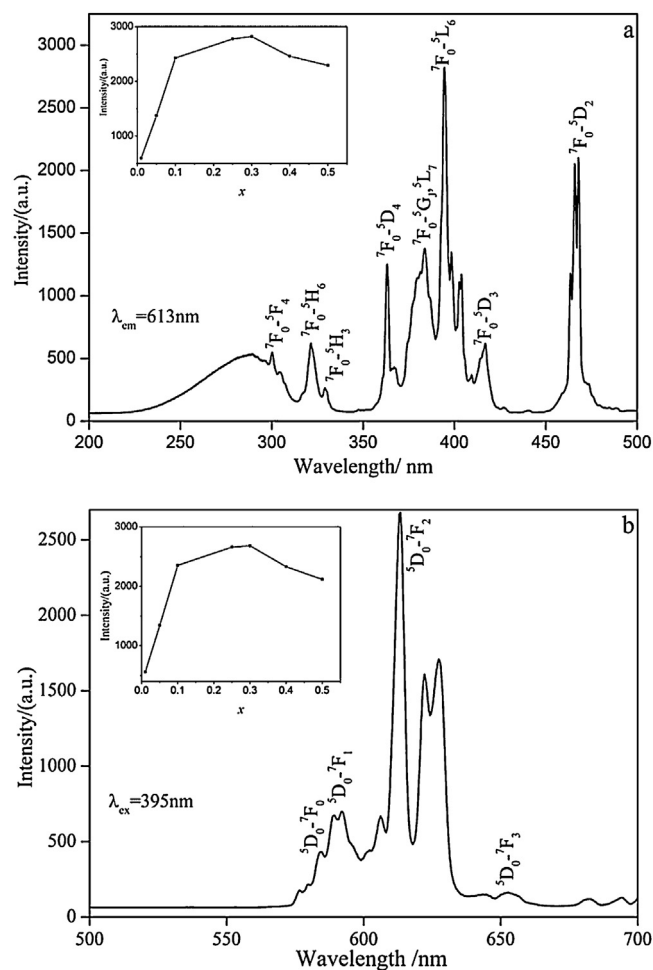
(99.50%),  $\text{Y}_2\text{O}_3$  (99.99%),  $\text{Eu}_2\text{O}_3$  (99.99%), and  $\text{Sm}_2\text{O}_3$  (99.99%) were used as raw materials, which were weighted precisely in proportion, thoroughly mixed, and ground to fine particle in an agate mortar. The fully mixed raw materials were placed inside corundum crucibles for heating. The mixtures were preheated at  $700^\circ\text{C}$  in air for 5 h followed by cooling at room temperature and grinding. Then they were fired at  $950^\circ\text{C}$  again for 5 h in air and cooled down to room temperature. Finally, the powders were washed with dilute nitric acid and deionized water several times to remove impurity and then dried at  $80^\circ\text{C}$  for 12 h.

The powders were characterized by X-ray diffraction (XRD) on a Bruker D8 advanced equipment ( $x$ ) using Cu tube with  $K\alpha$  radiation of  $0.15406\text{ nm}$  in the  $2\theta$  range of  $20^\circ$ – $80^\circ$ . The excitation and emission spectra of the samples were measured at room temperature using a Perkin-Elmer LS-50 luminescence spectrometer with a xenon flash lamp.

### 3. Results and discussion

In order to characterize the phase purity of the as-prepared powder samples, the XRD patterns for the samples with different Li/Y ratios were examined. The XRD patterns of the as-synthesized  $\text{Li}_g\text{Y}_{4.2}\text{O}_5(\text{BO}_3)_3:0.3\text{Eu}^{3+}$  ( $g=0, 0.3, 0.9, 1.5, 3,$  and  $4.5$ ) phosphors are shown in Fig. 1. The lithium yttrium borate  $\text{LiY}_6\text{O}_5(\text{BO}_3)_3$  has been demonstrated to be isostructural with  $\text{LiGd}_6\text{O}_5(\text{BO}_3)_3$  (PDF#89-4434) [13,15]. Therefore, the standard XRD patterns of  $\text{LiGd}_6\text{O}_5(\text{BO}_3)_3$  can be used as a contrast to examine the prepared  $\text{LiY}_6\text{O}_5(\text{BO}_3)_3$  samples in our experiment. At a low Li/Y ratio ( $<1/6$ ),  $\text{Y}_2\text{O}_3$  impurity can be observed. The pattern becomes increasingly close to that of  $\text{LiGd}_6\text{O}_5(\text{BO}_3)_3$  with the increase in the Li/Y concentration ratio. When the ratio is  $3/6$ , the diffraction peak is very close to the standard spectra of  $\text{LiGd}_6\text{O}_5(\text{BO}_3)_3$ , although the diffraction peaks of  $\text{LiY}_6\text{O}_5(\text{BO}_3)_3$  slightly shift toward high angles as compared with  $\text{LiGd}_6\text{O}_5(\text{BO}_3)_3$  as the  $\text{Y}^{3+}$  radius is smaller than the  $\text{Gd}^{3+}$  radius. The result indicates that the excess of  $\text{Li}_2\text{CO}_3$  can act as flux and help to form the target powder at relatively low temperature, which improves the synthesis method of  $\text{LiY}_6\text{O}_5(\text{BO}_3)_3$ .

It is believed that the electric-dipole transitions within the  $4f$ – $4f$  intra-configuration of rare earth ions only take place when the rare earth ions occupy the sites in the host without central symmetry. The rare earth ions in the  $\text{LiY}_6\text{O}_5(\text{BO}_3)_3$  host occupy the  $\text{C}_1$  sites of  $\text{Y}^{3+}$  ions with no inversion symmetry. Thus, efficient luminescence of trivalent rare earth ions in the  $\text{LiY}_6\text{O}_5(\text{BO}_3)_3$  host is expected.



**Fig. 2.** (a) Excitation ( $\lambda_{em} = 613\text{ nm}$ ) and (b) emission ( $\lambda_{ex} = 395\text{ nm}$ ) spectra of  $\text{LiY}_{4.2}\text{O}_5(\text{BO}_3)_3:0.3\text{Eu}^{3+}$  phosphors; the insets show the concentration-dependent excitation (395-nm)/emission (613-nm) intensity of the  $\text{LiY}_{4.2}\text{O}_5(\text{BO}_3)_3:\text{Eu}^{3+}$  sample.

The excitation spectra of  $\text{LiY}_{6(1-x)}\text{O}_5(\text{BO}_3)_3:x\text{Eu}^{3+}$  ( $x=0.01, 0.05, 0.1, 0.25, 0.3, 0.4,$  and  $0.5$ ) phosphors by monitoring  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  ( $\lambda_{em} = 613\text{ nm}$ ) emission are all measured. Fig. 2(a) shows the excitation spectra of the  $\text{LiY}_{4.2}\text{O}_5(\text{BO}_3)_3:0.3\text{Eu}^{3+}$  phosphor. It can be seen clearly that the excitation spectra consist of a broad band and a group of sharp peaks in the visible and UV region. The broad excitation band from 260 to 280 nm can be attributed to the charge transfer band (CTB) of  $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$  [16], and the other sharp peaks at wavelengths 300, 321, 329, 363, 383, 395, 417, and 465 nm can be attributed to the transitions of  ${}^7\text{F}_0$  to  ${}^5\text{F}_4$ ,  ${}^5\text{H}_6$ ,  ${}^5\text{H}_3$ ,  ${}^5\text{D}_4$ ,  ${}^5\text{G}_1$  ( ${}^5\text{L}_7$ ),  ${}^5\text{L}_6$ ,  ${}^5\text{D}_3$ , and  ${}^5\text{D}_2$ , respectively [17]. The  $\text{LiY}_6\text{O}_5(\text{BO}_3)_3:\text{Eu}^{3+}$  phosphors with different  $\text{Eu}^{3+}$  concentrations present similar excitation spectra except for the difference in intensity. The inset in Fig. 2(a) shows the  $\text{Eu}^{3+}$  concentration-dependent excitation intensity at 395 nm. It is found that the strongest excitation intensity appears at  $x=0.3$ . Importantly, the phosphors have strong excitation bands at 375–405 nm, which matches with the emission wavelengths of NUV LED chips.

The emission spectra of the  $\text{LiY}_{4.2}\text{O}_5(\text{BO}_3)_3:0.3\text{Eu}^{3+}$  phosphor under 395-nm excitation are shown in Fig. 2(b), and the emission intensity as a function of  $\text{Eu}^{3+}$  concentration is also given as an inset in Fig. 2(b). The emission spectra are composed of a group of sharp peaks originating from the  $\text{Eu}^{3+}$  intra-configuration  $4f$ – $4f$  transitions  ${}^5\text{D}_0$  to  ${}^7\text{F}_0$ ,  ${}^7\text{F}_1$ ,  ${}^7\text{F}_2$ , and  ${}^7\text{F}_3$  at 584, 592, 613, and 652 nm, respectively [18]. Under excitation of 395 nm, the phosphor exhibits strong red emission band peaking at 613 nm. The

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