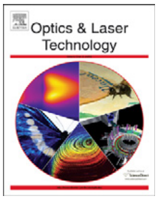
Optics & Laser Technology 46 (2013) 14–19

Contents lists available at SciVerse ScienceDirect

Optics & Laser Technology

journal homepage: www.elsevier.com/locate/optlastec



# Photoluminescence properties of novel red-emitting $NaSrBO_3:Eu^{3+}$ phosphor for near-UV light-emitting diodes

Fan Yang [a,b], Yujun Liang [a,b,*], Mingyu Liu [b], Xuejing Li [b], Mengfei Zhang [b], Nan Wang [b]

[a] *Engineering Research Center of Nano-Geomaterials of Ministry of Education, China University of Geosciences, Wuhan 430074, People's Republic of China*
[b] *Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan 430074, People's Republic of China*

## ARTICLE INFO

*Article history:*
Received 4 February 2012
Received in revised form
12 April 2012
Accepted 13 April 2012
Available online 15 June 2012

*Keywords:*
Borates
Concentration quenching
Near-UV LED

## ABSTRACT

A series of $NaSrBO_3:xEu^{3+}$ and $NaSr_{1-2x}BO_3:xEu^{3+}$, $xM^+$ (M=Li, Na, K) phosphors were synthesized by the solid state reaction. The crystal structure, photoluminescence properties and concentration quenching of $NaSrBO_3:Eu^{3+}$ phosphors were systematically investigated. The excitation spectra indicate that the phosphors can be efficiently excited by 394 nm, which is matched well with the emission wavelength of near-UV LED chip. All the samples show the characteristic red emission of $Eu^{3+}$ ions ($^5D_0 \rightarrow {}^7F_J$, $J=0$, 1, 2, 3 and 4). The maximum intensity of luminescence is observed at the $Eu^{3+}$ concentration around $x=0.11$. The concentration quenching of $Eu^{3+}$ in $NaSrBO_3:Eu^{3+}$ phosphor can be mainly attributed to quadrupole–quadrupole interaction. The relative emission intensities of $Eu^{3+}$ ($^5D_0 \rightarrow {}^7F_2$) in $NaSrBO_3:Eu^{3+}$ phosphors with $Li^+$, $Na^+$ or $K^+$ introduced as charge compensator are significantly enhanced, and the phosphors added with $K^+$ ions show the strongest emission. The emission intensities of $NaSr_{1-2x}BO_3:xEu^{3+}$, $xM^+$ (M=Li, Na, K) are about 1.47, 1.64 and 2.08 times than that of commercial red phosphor $Y_2O_2S:Eu^{3+}$. These results indicate that $NaSr_{1-2x}BO_3:xEu^{3+}$, $xM^+$ (M=Li, Na, K) phosphors exhibit potential applications in the field of near-UV LED as an efficient red-emitting phosphors.

## 1. Introduction

White light-emitting diode (W-LED) is considered to be the fourth generation illumination lamp over the conventional incandescent and halogen lamp due to advantages of saving-energy, environment protection, long lifetime, reliability [1–3]. Currently, there are mainly two approaches to produce white light. one approach to achieve white light which has become a commercial production in large-scale is to combine cerium-doped yttrium aluminum garnet (YAG:Ce) phosphors with blue InGaN chip, in which a blue light-emitting InGaN chip is used to excite phosphors which emit yellow light and then mix the remaining blue light from the pump to compose desired white light [4]. However, low color rendering index (CRI) due to lack of red component limits the applicability for this type of LED [4–6]. In order to improve the white light quality, the other approach to obtain white light is proposed to combine UV LED chip with multi-phased (red, green and blue) phosphors, which possesses high color rendering index and superior color uniformity due to white color generated only by phosphors [7,8]. However, the main red-emitting phosphor for UV LED chip is $Y_2O_2S:Eu^{3+}$ which shows chemical instability and low absorption efficiency in the near UV region [9,10]. Therefore, it is highly desirable to develop a new stable phosphor that can emit intense red emission with strong excitation band at around 400 nm for near-UV LED chip.

Borates have been extensively investigated due to their high thermal, chemical stability and strong absorption in the near ultraviolet region. Rare earth doped borate phosphors have considerable practical applications in various devices such as solid-state lasers, optical communication, Plasma display panel (PDP), and LED [11–13]. Among the borates, the crystal structure of $NaSrBO_3$ was first reported by Wu et al. [14]. Until recently, Liu WR et al. have synthesized a high efficiency and high color purity blue-emitting $NaSrBO_3:Ce^{3+}$ phosphor and also investigated the luminescence properties, thermal stability and the application in UV LEDs [15]. However, to the best of our knowledge, there is no report devoted to the photoluminescence properties of $Eu^{3+}$-activated $NaSrBO_3$ phosphors in the literature until now.

In this study, a novel phosphor $NaSrBO_3:xEu^{3+}$ has been prepared. The photoluminescence excitation and emission spectra, concentration quenching of $NaSrBO_3:xEu^{3+}$ phosphor were studied. The alkali metal ions such as $Li^+$, $Na^+$ or $K^+$ were introduced as charge compensators to enhance the red emission intensity of the $Eu^{3+}$ doped $NaSrBO_3$. The effects of the charge compensation on the luminescent properties of the phosphors doped with different alkali

---

[*] Corresponding author at: Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan 430074, China. Tel.: +86 27 67884814; fax: +86 27 67883733.
*E-mail address:* yujunliang@sohu.com (Y. Liang).

0030-3992/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.optlastec.2012.04.015

metal ions are investigated. Furthermore, the performance of our phosphors is also compared to the commercial red phosphors $Y_2O_2S:Eu^{3+}$. The results demonstrated that $NaSr_{1-2x}BO_3:xEu^{3+}$, $xM^{+}$ (M=Li, Na, K) is a potential red-emitting phosphor for near-UV LED.

## 2. Experimental

A series of $Eu^{3+}$-activated $NaSrBO_3$ powder samples were synthesized by the conventional solid state reaction. $Na_2CO_3$ (99.9%), $SrCO_3$ (99.9%) $Eu_2O_3$ (99.99%) and $H_3BO_3$ (A.R.) were used as raw materials. The stoichiometric amounts of starting materials were weighted and thoroughly mixed in an agate mortar, the mixtures then were put in an alumina crucible and calcined at 850 °C for 8 h in air. In some cases, appropriate amounts of $Li_2CO_3$ (99.9%), $Na_2CO_3$ (99.9%), $K_2CO_3$ (99.9%) were added as charge compensators. The $Y_2O_2S:Eu^{3+}$ phosphor was prepared according to Ref. [16].

The crystal structure of the phosphors were characterized by X-ray powder diffractometer (XRD) (Bruker D8 Focus) with Ni-filtered Cu-kα ($\lambda$=1.540598 Å) radiation at 40 kV tube voltage and 40 mA tube current. The morphology and microstructure were characterized with Japan JSM-35CF environmental scanning electron microscope (SEM) at 20 kV. The XRD data were collected in a 2θ range from 10° to 70°, with the continuous scan mode at the speed of 0.05 s per step with step size of 0.01°. Excitation and emission spectra were measured by fluorescence spectrometer (FLUOROMAX-4) equipped with a 150 W xenon lamp as the excitation source. The excitation spectra were obtained by scanning from 200 to 500 nm monitored at 611 nm. The emission spectra were scanned from 500 to 750 nm excited at 394 nm, respectively. The spectral resolution of both excitation and emission spectra was set up to be 1.0 nm with the width of the monochromator slits adjusted as 0.50 nm. The other measurement conditions (PMT detector sensitivity, scan peed) were kept consistent from sample to sample in measurements. All the measurements were carried out at room temperature.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of $Y_2O_2S:0.05Eu^{3+}$, $NaSrBO_3$: $xEu^{3+}$ and $NaSr_{1-2x}BO_3:xEu^{3+}$, $xM^{+}$ ($x$=0.11, M=Li, Na, K). The curve (a) shows that $Y_2O_2S:0.05Eu^{3+}$ is consistent with JCPDS 24-1424 ($Y_2O_2S$) without other impurity phase. The XRD patterns of $NaSrBO_3:0.11Eu^{3+}$ (b) and $NaSr_{0.78}BO_3:0.11Eu^{3+}$, $0.11M^{+}$ (M=Li, Na, K) (c, d, e) exhibit the same diffraction peaks as appeared in $NaSrBO_3$ ICSD standard pattern corresponding to the monoclinic structure with space group of $P2_1/c$. The reported lattice parameters of $NaSrBO_3$ are $a$=5.32446(7) Å, $b$=9.2684(1) Å, $c$=6.06683(8) Å and $\beta$=100.589(1)°. The cell volume ($V$) and cations in the unit cell ($Z$) are 294.30(8) $Å^3$ and 4. In $NaSrBO_3$ crystal lattice, the fundamental building units are isolated planar $BO_3$ anionic groups, which are parallelly distributed along two different directions. The Na atoms are six-coordinated with O atoms to form octahedra, and the Sr atoms coordinated by nine O atoms are in the form of tri-capped trigonal prisms [14]. As we all know, the ionic radius of $Eu^{3+}$ ($r$=1.12 Å, CN=9) is close to that of $Sr^{2+}$ ($r$=1.31 Å, CN=9). The six-coordinated $Na^{+}$ ($r$=1.02 Å) sites and three-coordinated $B^{3+}$ ($r$=0.39 Å) sites are too small for $Eu^{3+}$ to occupy [17]. Based on the effective ionic radius of cations with different coordination numbers, it is assumed that $Eu^{3+}$ ions are preferably to replace $Sr^{2+}$ ions. Generally, when a metal cation substitutes for an ion with different valence in host lattice, charge compensator such as $Li^{+}$, $Na^{+}$ or $K^{+}$ is employed to keep charge balance. The charge compensation in above mentioned structure can be described by two possible mechanisms: (1) two $Sr^{2+}$ ions are replaced by one $Eu^{3+}$ ions and one alkaline cation, $2Sr^{2+} \rightarrow Eu^{3+} + M^{+}$, where $M^{+}$ is an alkaline cation like $Li^{+}$, $Na^{+}$ or $K^{+}$; (2) the charge compensation is provided by a strontium vacancy, $3Sr^{2+} \rightarrow 2Eu^{3+} + V_{Sr}$.

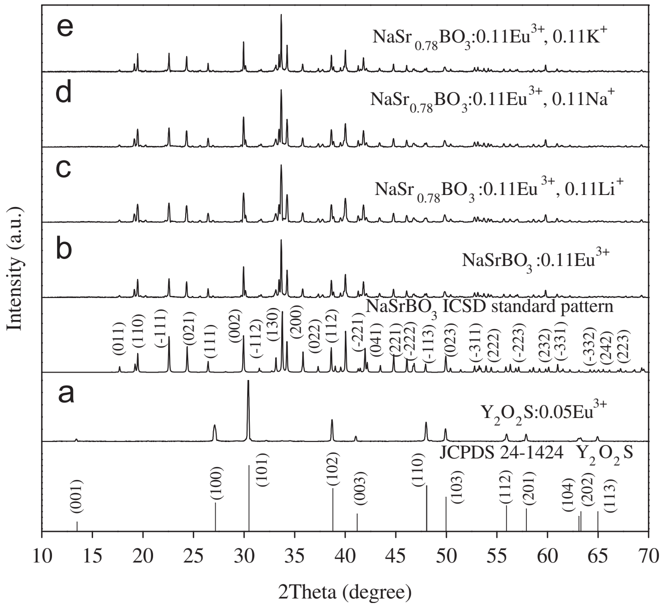


**Fig. 1.** XRD patterns of $NaSrBO_3:xEu^{3+}$, $NaSr_{1-2x}BO_3:xEu^{3+}$, $xM^{+}$ ($x$=0.11, M=Li, Na, K) and $Y_2O_2S:0.05Eu^{3+}$, with the $NaSrBO_3$ ICSD standard pattern, $Y_2O_2S$ (JCPDS 24-1424).

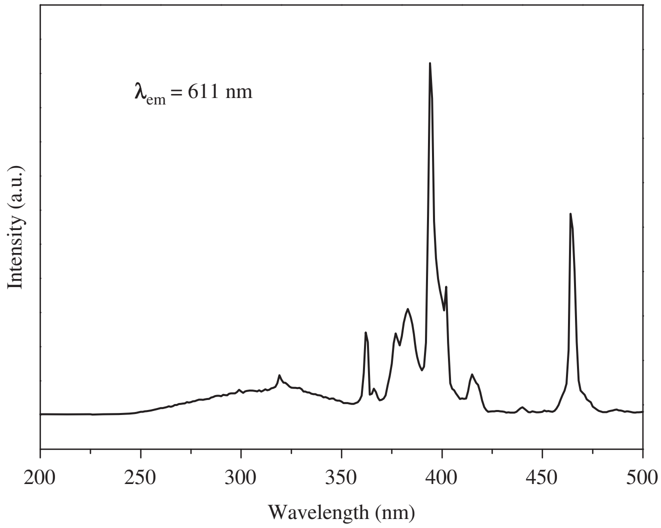


**Fig. 2.** Photoluminescence excitation spectrum of $NaSrBO_3:0.11Eu^{3+}$.

Fig. 2 presents the photoluminescence excitation spectrum of $NaSrBO_3:0.11Eu^{3+}$ monitored at 611 nm. The excitation spectrum exhibits a weak broad band from 250 to 350 nm ascribed to O–Eu charge-transfer band (CTB) transition and the other peaks in the range of 350–500 nm originated from f–f transitions of $Eu^{3+}$ ions. The strongest band at 394 nm can be assigned to $^7F_0 \rightarrow {}^5L_6$ transition of $Eu^{3+}$ ions. In any case, it is a good phenomenon that the as-prepared phosphors can strongly absorb the ultraviolet light, which is matched well with the characteristic emission of the near-UV LED chips.

The emission spectra of $NaSrBO_3$ doped with different $Eu^{3+}$ concentrations are shown in Fig. 3. All of the emission spectra exhibit the similar profile with different relative intensities. Each