A novel yellow phosphor for white light emitting diodes*

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This paper reports that a novel yellow phosphor, $LiSrBO_3:Eu^{2+}$, was synthesized by the solid-state reaction. The excitation and emission spectra indicate that this phosphor can be effectively excited by ultraviolet (360 and 400 nm) and blue (425 and 460 nm) light, and exhibits a satisfactory yellow performance (565 nm). The role of concentration of Eu^{2+} on the emission intensity in $LiSrBO_3$ is studied, and it is found that the critical concentration is 3 mol%, and the concentration self-quenching mechanism is the dipole–dipole interaction according to the Dexter theory. White light emitting diodes were generated by using an InGaN chip (460 nm or 400 nm) with $LiSrBO_3:Eu^{2+}$ phosphor, the CIE chromaticity is ($x = 0.341$, $y = 0.321$) and ($x = 0.324$, $y = 0.318$), respectively. Therefore, $LiSrBO_3:Eu^{2+}$ is a promising yellow phosphor for white light emitting diodes.

Keywords: luminescence, white light emitting diodes, $LiSrBO_3:Eu^{2+}$

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1. Introduction

Recently, there has been considerable interest in the development of white light emitting diodes (LEDs) using GaN as well as an InGaN chip.[1−2] Recently, in particular, white LEDs in which a blue LED is combined with a yellow YAG:Ce phosphor were extensively investigated due to their applications, such as backlighting for liquid crystal displays and incandescent lamps.[3] There have been some detailed studies on the integration of the blue LED and the yellow phosphor. The phosphor conversion of LED light for white light strongly depends on the strong absorption of the blue LED emission wavelength. The strong absorption can be expected from dipole-allowed electron transitions in activated ions. The ions Ce^{3+} and Eu^{2+} are well known activated ions, which can be shifted by crystal field in the spectral location of their absorption and emission lines. Some research results have already been reported in this region, such as $Ca_3SiO_5:Eu^{2+}$ and $Sr_6BP_5O_{20}:Eu^{2+}$ green phosphor, $Sr_2SiO_4:Eu^{2+}$ yellow-green phosphor, $Sr_3SiO_5:Eu^{2+}$ yellow phosphor, $Sr_3MgSi_2O_8:Eu^{2+}$, $Sr_2MgSiO_5:Eu^{2+}$ and $Sr_3B_2O_6:Ce^{3+}$, Eu^{2+} white phosphor.[4−10] However, very few efficient new yellow phosphors have actually been discovered, in addition to YAG:Ce phosphor, silicate phosphor and some organic luminescent materials.[11]

Hence, we have attempted to develop a yellow phosphor that emits efficiently under the 450–470 nm excitation range. In the present work, Eu^{2+}-activated $LiSrBO_3$ yellow phosphor was synthesized and its luminescence characteristics were studied. White LED through the integration of the InGaN chip (460 nm or 400 nm) and the $LiSrBO_3:Eu^{2+}$ phosphor into a single package was developed.

2. Experiment

$LiSrBO_3:Eu^{2+}$ phosphors were synthesized through the solid-state reaction. The starting materials were $SrCO_3$ (99.9%), H_3BO_3 (99.9%), Li_2CO_3 (99.9%) and Eu_2O_3 (99.9%). After these individual materials were ground thoroughly in an agate mortar, the homogeneous mixture was heated at 700 °C for 2 h in a reducing atmosphere (a mixture of 5 % H_2 and 95% N_2), and then $LiSrBO_3:Eu^{2+}$ phosphors were obtained.

The presented phase of the samples was characterized by powder x-ray diffraction (XRD) (D/max-rA, Cu Kα, 40 kV, 40 mA, $\lambda = 0.15406$ nm). The emission and excitation spectra were measured by a SHIMADZU RF-540 fluorescence spectrophotometer. All the luminescence characteristics of these phosphors were investigated at room temperature.

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3. Results and discussion

3.1. Structure of $LiSrBO_3$:Eu^{2+} phosphor

Figure 1 shows the XRD pattern of $LiSrBO_3$:Eu^{2+} phosphor with 1 mol% Eu^{2+}. All patterns agree well with Ref. [12], indicating that the doped Eu^{2+} ions have not caused any significant changes in the host structure. $LiSrBO_3$ has a monoclinic structure with $P2_1/n$ space group, and the values of the lattice parameters are $a = 0.6476$ nm, $b = 0.6684$ nm and $c = 0.6843$ nm.

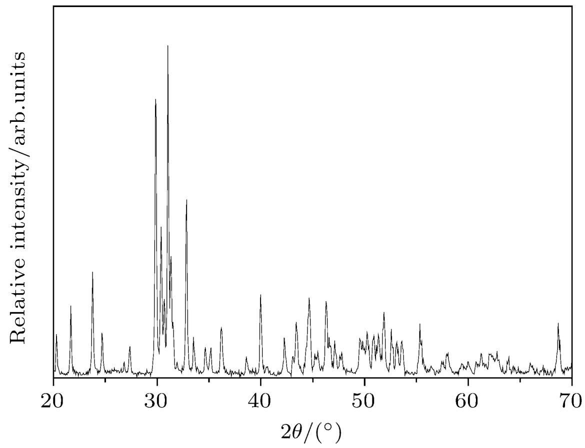

Fig. 1. The XRD pattern of $LiSrBO_3$:Eu^{2+} phosphor.

3.2. Emission and excitation spectra of $LiSrBO_3$:Eu^{2+} phosphor

In Fig. 2, under the 460 nm excitation, $LiSrBO_3$:Eu^{2+} phosphor exhibits a broad band at 565 nm. However, another emission band located at 487 nm was observed under 400 nm excitation. Monitoring at 565 nm, we find that the excitation spectrum extends from 300 nm to 500 nm, and the peaks locate at 360, 400, 425 and 460 nm, respectively. Therefore, $LiSrBO_3$:Eu^{2+} phosphor can emit efficiently under 460 nm excitation which makes it possible to create white light from a combination of a blue LED ($\lambda_{em} = 460$ nm) like YAG:Ce phosphor, and the emission of YAG:Ce phosphor can be seen from the inset of Fig. 2.

Comparing $LiSrBO_3$:Eu^{2+} with YAG:Ce phosphor, we find that the emission intensity of $LiSrBO_3$:Eu^{2+} phosphor is appreciably higher than that of YAG:Ce phosphor under the same excitation wavelength and intensity. Moreover, the emission wavelength of $LiSrBO_3$:Eu^{2+} phosphor is longer than that of YAG:Ce phosphor. Therefore, a white LED which can be fabricated by combining 460 nm InGaN chip with $LiSrBO_3$:Eu^{2+} phosphor may have better characteristics than that of an InGaN chip based YAG:Ce phosphor. Hence, $LiSrBO_3$:Eu^{2+} is a promising yellow phosphor for white LEDs.

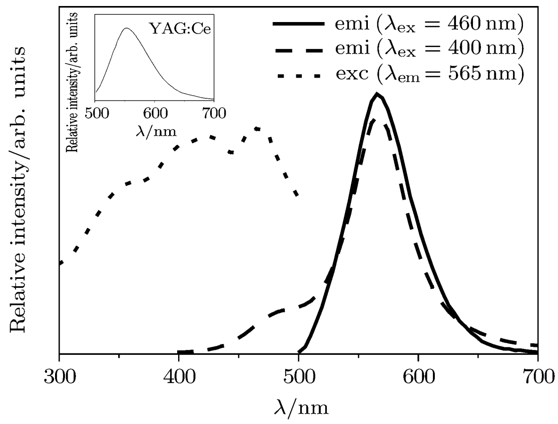

Fig. 2. Emission and excitation spectra of $LiSrBO_3$:Eu^{2+} phosphor, and the emission spectra under 400 or 460 nm excitation. The inset shows the emission spectrum of YAG:Ce phosphor under 460 nm excitation..

3.3. Effect of Eu^{2+} concentration on emission spectra of $LiSrBO_3$:Eu^{2+} phosphor

The emission intensities of $LiSrBO_3$:Eu^{2+} phosphors as a function of Eu^{2+} concentration are shown in Fig. 3 under 460 nm excitation. The results show that the emission intensity initially increases with increasing Eu^{2+} concentration, and reaches a maximum at 3 mol% Eu^{2+}. A decrease in the emission intensity is observed as the Eu^{2+} concentration increases, and this shows the occurrence of energy migration between Eu^{2+} in different sites in the lattice, resulting in concentration quenching. Nonradiative energy transfer from one Eu^{2+} ion to another Eu^{2+} ion usually occurs by exchange interaction, radiation reabsorption or multipole–multipole interaction. In the case of the Eu^{2+} ion, the $4f^7 \rightarrow 4f^6 5d^1$ transition is allowed, while exchange interaction is responsible for energy transfer for forbidden transitions with a typical critical distance, which is about 5 Å (1 Å=0.1 nm).[13] Therefore, the energy transfer in the present case will occur only by electric multipolar interaction. The value of the critical transfer distance (R_c) can be obtained from Dexter's formula for energy transfer by the electric dipole–dipole interaction.

$$R_c^6 = 0.63 \times 10^{28} \times 4.8 \times 10^{-16} P_A \times E^{-4} \times \text{S.O.}$$

In Ref. [14], the physical meaning of P_A, E and S.O. were introduced. By the adoption of these values and calculated spectral overlap, the critical distance (R_c) value of energy transfer between the Eu^{2+} ion and the Eu^{2+} ion was estimated to be 18.5 Å. It could be confirmed that the energy transfer of Eu^{2+}–Eu^{2+} ions in $LiSrBO_3$ occurs by multipolar interaction through the calculated R_c.

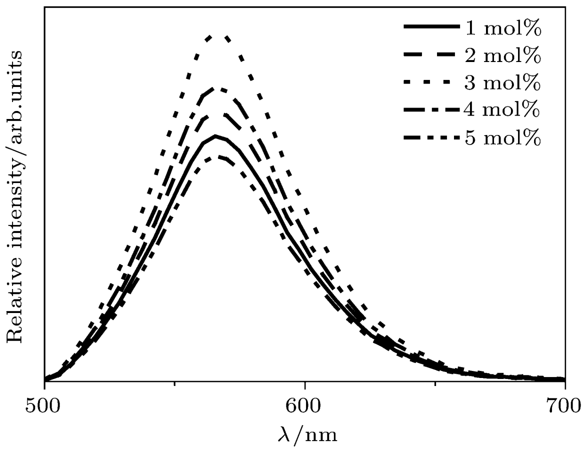

Fig. 3. Emission intensity of $LiSrBO_3$:Eu^{2+} phosphor as function of Eu^{2+} concentration.

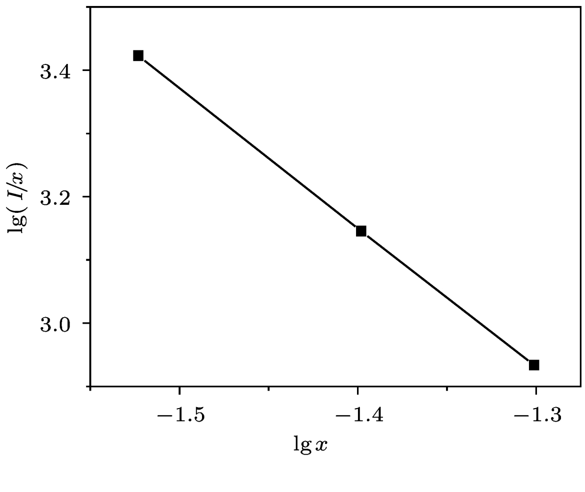

Fig. 4. Relation between the lg(I/x) and lg$x$ of Eu^{2+}.

Dexter[15] proposed that the interaction type between sensitizers or between sensitizer and activator can be determined by $\lg(I/x) = c - (\theta/3)\lg x$ when the concentration is high enough. Among the concentration quenching mechanisms caused by the electric multipole interaction, dipole–dipole (d–d), dipole–quadripole (d–q) and quadripole–quadripole (q–q) interactions correspond to $\theta = 6$, 8 and 10, respectively. The quantity I is the luminescence intensity of $LiSrBO_3$:Eu^{2+} phosphor, and x is the Eu^{2+} concentration. According to the formula, the emission intensities of $LiSrBO_3$:Eu^{2+} phosphors were measured with Eu^{2+} concentrations of 3, 4 and 5 mol%, and the concentration dependence curves ($\lg(I/x)$–$\lg x$) are shown in Fig. 4. According to the linear slope, $\theta = 5.89 \approx 6$. This result indicates that the concentration self-quenching mechanism of Eu^{2+} in $LiSrBO_3$ is the d–d interaction.

3.4. Relative emission spectra of InGaN-based $LiSrBO_3$:Eu^{2+} phosphor

The relative emission spectrum of the InGaN chip (460 nm)-based $LiSrBO_3$:Eu^{2+} LED is shown in Fig. 5. The InGaN-based $LiSrBO_3$:Eu^{2+} LED shows two distinct emissions from the InGaN-based LED and the $LiSrBO_3$:Eu^{2+} phosphors are clearly around at 460 nm and 565 nm, respectively. The 460 nm emission band is due to a radiative recombination from an InGaN active layer. This blue emission was used as an optical transition of $LiSrBO_3$:Eu^{2+} phosphor. The 565 nm emission band is ascribed to Eu^{2+} impurity ion emission in the $LiSrBO_3$ host matrix. It is presumed that energy from the 460 nm excitation band may be trapped at the Eu^{2+} ion and emits a yellow emission at 565 nm. These two bands combine to give a spectrum which appears to be white to the naked eye, and the Coommission Internationale de l'Eclairage (CIE) chromaticity is ($x = 0.341$, $y = 0.321$).

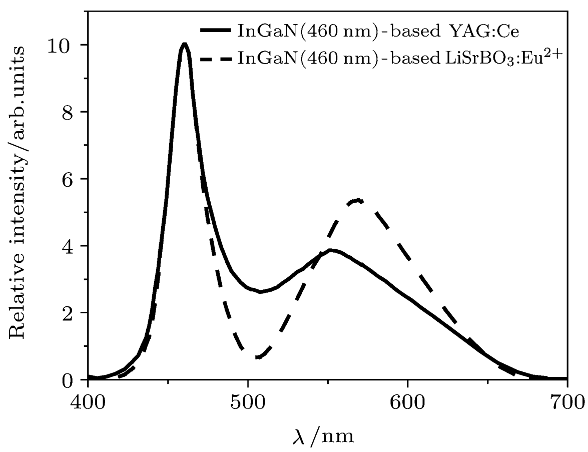

Fig. 5. Relative emission spectra of a white light emitting InGaN-based $LiSrBO_3$:Eu^{2+} LED and an InGaN-based YAG:Ce LED.

Comparing the relative emission of InGaN-based $LiSrBO_3$:Eu^{2+} with that of InGaN-based YAG:Ce, we find that the emission intensity of $LiSrBO_3$:Eu^{2+}

phosphor is higher than that of YAG:Ce phosphor under the same InGaN LED chip. Moreover, the emission wavelength of $LiSrBO_3:Eu^{2+}$ phosphor is longer than that of YAG:Ce phosphor. The luminous efficiency of the InGaN-based $LiSrBO_3:Eu^{2+}$ LED measured from these results is about 13–15 lm/W, which is higher than that of the industrially available InGaN-based YAG:Ce (in this case, 12 lm/W).

The relative emission spectrum of the InGaN chip (400 nm)-based $LiSrBO_3:Eu^{2+}$ LED is illuminated in Fig. 6, and its emission spectrum shows two distinct emission bands. The 400 nm emission band is due to a radiative recombination from an InGaN active layer. The 565 nm emission band is ascribed to Eu^{2+} emission in the $LiSrBO_3$ host matrix. It is presumed that energy from the 400 nm excitation band may be trapped at the Eu^{2+} ion and emits a yellow emission at 565 nm. The broad band combines to give a spectrum that appears to be white to the naked eye, and

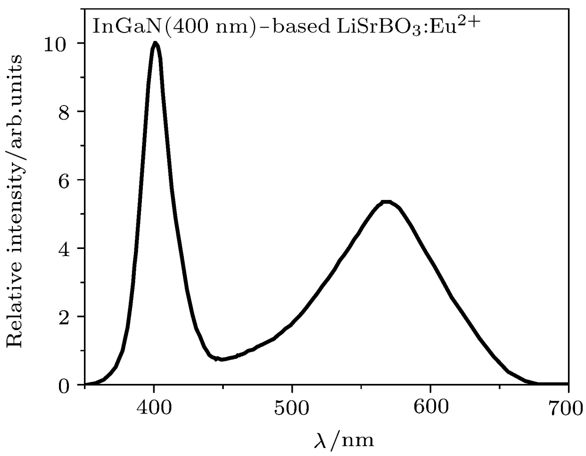

Fig. 6. Relative emission spectra of a white light emitting InGaN (400 nm)-based $LiSrBO_3:Eu^{2+}$ LED.

the CIE chromaticity is (x = 0.324, y = 0.318). All these results show that $LiSrBO_3:Eu^{2+}$ is a promising yellow phosphor for white LEDs.

3.5. Temperature dependence of $LiSrBO_3:Eu^{2+}$ and YAG:Ce phosphors

Changing the temperature of the LED pn junction leads to changing light output, wavelength, and spectral width.[16] It is noted, therefore, that temperature dependence of the phosphor is very important. The temperature dependence of the emission intensities of $LiSrBO_3:Eu^{2+}$ and YAG:Ce phosphor between 25 °C and 200 °C are shown in Fig. 7. At low temperature (< 100 °C), the emission intensities of these two phosphors were stable with increasing temperature, the emission intensities are decreased due to temperature quenching, however, the emission intensities of $LiSrBO_3:Eu^{2+}$ phosphor measured from these results are close to those of YAG:Ce phosphor. Therefore, $LiSrBO_3:Eu^{2+}$ phosphor is a stable phosphor for white LEDs.

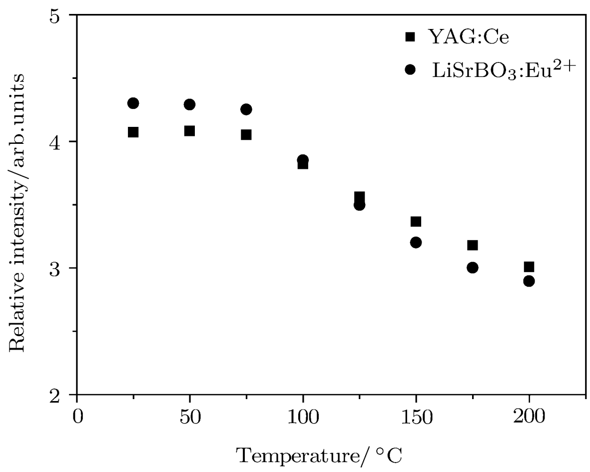

Fig. 7. Temperature dependence of the emission intensities of $LiSrBO_3:Eu^{2+}$and YAG:Ce phosphor.

4. Conclusions

In summary, the yellow $LiSrBO_3:Eu^{2+}$ phosphor was investigated. The combination of an InGaN chip (460 nm or 400 nm) and a broad band yellow $LiSrBO_3:Eu^{2+}$ phosphor creates a white line, and the CIE chromaticity is (x = 0.341, y = 0.321) and (x = 0.324, y = 0.318), respectively. Therefore, $LiSrBO_3:Eu^{2+}$ is a promising yellow phosphor for white LEDs.

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