Sr 3 B 2 O 6 : Ce 3 + , Eu 2 + : A potential single-phased white-emitting borate phosphor for ultraviolet light-emitting diodes

Chun-Kuei Chang and Teng-Ming Chen

Sr$_3$B$_2$O$_6$:Ce^{3+},Eu^{2+}: A potential single-phased white-emitting borate phosphor for ultraviolet light-emitting diodes

Chun-Kuei Chang and Teng-Ming Chen[a)]

Phosphors Research Laboratory, National Chiao Tung University, Hsinchu 30010, Taiwan
and Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30010, Taiwan

The Ce^{3+}/Eu^{2+} coactivated Sr$_3$B$_2$O$_6$ phosphors exhibit varied hues from blue through white and eventually to yellow-orange by resonance-type energy transfer from Ce^{3+} to Eu^{2+} and tuning the relative proportion of Ce^{3+}/Eu^{2+} properly. The authors have demonstrated that electric dipole-dipole interaction dominates the energy transfer mechanism in Sr$_3$B$_2$O$_6$:Ce^{3+},Eu^{2+} phosphor, and the critical distance of energy transfer has been estimated to be about 30 Å by both spectral overlap and concentration quenching methods. They have also shown that under the excitation of UV radiation, white light is generated by coupling 434 and 574 nm emission bands attributed to Ce^{3+} and Eu^{2+} radiations, respectively. © 2007 American Institute of Physics. [DOI: 10.1063/1.2772195]

A primitive white LED lamp consisting of three LED dices of red, green as well as blue is easy to fabricate, but some disadvantages exist: (1) high cost, (2) drive voltages are different to each other, and (3) thermal properties and degradation trends are also different, and, thus, restrict its wide application. A good choice to assemble white LEDs in low cost is to couple a blue or near-ultraviolet (UV) LED with a downconverting phosphor. For example, the commercial YAG (yttrium aluminum garnet):Ce (Ref. 1) yellow phosphor excited by a blue GaN LED results in two-band white light emission. In spite of white light that is easily achieved in YAG:Ce based system, the individual degradation rate between the blue LED and yellow phosphor will cause chromatic aberration and poor white light performance after long period of working. Developing a single-phased white-emitting phosphor using the principle of energy transfer (ET) from a sensitizer (energy donor) to an activator (energy accepter) in a single host lattice for UV LEDs is an excellent option to replace YAG:Ce based white-emitting system. The ions possessing *f-d* or *d-d* electron configurations are good candidates to be selected as activators in phosphors because they could emit visible and broadband light under the influence of crystal-field and nephelauxectic effects.[2] Moreover, white light can be produced by codoping these ions together under effective resonance-type ET in a single host, such as Eu^{2+}/Mn^{2+} coactivated systems.[3–10] Although there were sweeping studies on Eu^{2+}/Mn^{2+} codoped white-emitting phosphors in the past years, yet, investigations on Ce^{3+}/Eu^{2+} codoping white-emitting phosphors were rarely reported. In certain Eu^{2+}-doped oxide matrices, the yellow-orange emission and UV to blue-light excitation are commonly observed through the strong crystal-field splitting and the lower energy of centroid of 5*d* level. Hence, Eu^{2+} can be sensitized by a well-known blue-emitting Ce^{3+} in such oxide lattices because of the spectral overlap between emission band of Ce^{3+} and excitation band of Eu^{2+}. Consequently, white light with blue and yellow-orange irradiations can be produced in this kind of Ce^{3+}/Eu^{2+}-codoped single-composition oxide host.

The crystal structure of Sr$_3$B$_2$O$_6$ was first determined and reported by Richter and Muller[11] in 1980; the luminescence of Sr$_3$B$_2$O$_6$:Ce^{3+} and Sr$_3$B$_2$O$_6$:Eu^{2+} was reported to exhibit blue and yellow-orange emissions, respectively, at 4.2 K by Schipper *et al.* in 1993.[12] However, the luminescence properties of Ce^{3+}/Eu^{2+}-codoped Sr$_3$B$_2$O$_6$ have not been reported in the literature. Therefore, according to the design principles discussed above, we have explored and discovered a single-composition Sr$_3$B$_2$O$_6$:Ce^{3+},Eu^{2+} (SBO:Ce,Eu) white phosphor and investigated its luminescence properties as well as ET phenomenon between the sensitizer and activator for potential application in white LEDs.

SBO:Ce,Eu phosphors studied in this work were synthesized by a solid-state reaction route. The reactants SrO, H$_3$BO$_3$, CeO$_2$, and Eu$_2$O$_3$ with high purity of 99.99% were mixed in the requisite proportions and calcined at 900–1000 °C under 15% H$_2$/Ar atmosphere. The detailed measurements of photoluminescence (PL), photoluminescence excitation (PLE), Commission International de I'Eclairage (CIE) chromaticity, and diffuse reflectance (DR) spectra have been carried out at room temperature and detailed in our previous work.[6]

The PL, PLE, and DR spectra for solely Ce^{3+} (or Eu^{2+})-doped and Ce^{3+}/Eu^{2+}-codoped Sr$_3$B$_2$O$_6$ are represented in Fig. 1. As shown in Fig. 1(a), under UV of 351 nm excitation, a broad asymmetric blue emission band centering at 434 nm, which is attributed to the $5d^1 \rightarrow 4f^1$ transition of Ce^{3+}, is observed in the PL spectrum. The asymmetry of the emission band of Sr$_3$B$_2$O$_6$:Ce^{3+} results from the spin-orbit coupling into two levels of ground state, and it can be deconvoluted into two Gaussians centering at 427 and 470 nm that originated from the lowest 5*d* level to $^2F_{5/2}$ and $^2F_{7/2}$, respectively. The energy difference between spin-orbit splitting of 4*f* ground state in Sr$_3$B$_2$O$_6$:Ce^{3+} is about 2142 cm^{-1} which is in good agreement with the theoretical value[13] of 2000 cm^{-1}. As depicted in Fig. 1(b), the PL spectrum of Sr$_3$B$_2$O$_6$:Eu^{2+} shows a broad yellow-orange emission band centering at 574 nm attributed to the typical $4f^65d^1 \rightarrow 4f^7(^8S_{7/2})$ transition of Eu^{2+}, and the PLE spectrum shows a broad absorption from UV to blue region with a maximum at 377 nm. The low energy of Eu^{2+} emission band in Sr$_3$B$_2$O$_6$:Eu^{2+} is due to the strong crystal-field and nephe-

[a)]Author to whom correspondence should be addressed; electronic mail: tmchen@mail.nctu.edu.tw

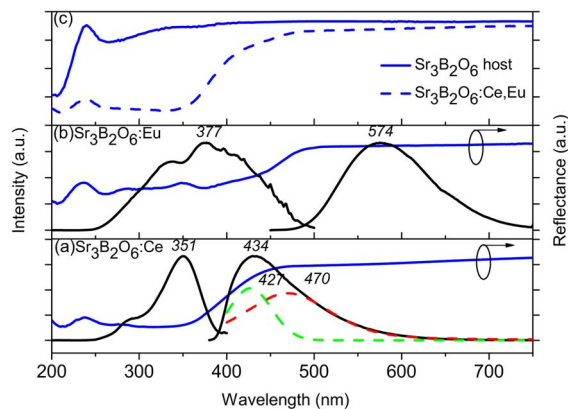FIG. 1. (Color online) PLE, PL, and DR spectra for (a) $Sr_3B_2O_6:Ce^{3+}$ phosphor (PLE monitored at 434 nm, PL excited at 351 nm, and DR spectra shown in blue curve), (b) $Sr_3B_2O_6:Eu^{2+}$ phosphor (PLE monitored at 574 nm, PL excited at 377 nm, and DR spectra shown in blue curve), and (c) DR spectra for $Sr_3B_2O_6$ host (blue solid line) and $Sr_3B_2O_6:Ce,Eu$ (blue dashed line). Spectral overlaps between PLE of $Sr_3B_2O_6:Eu^{2+}$ and PL of $Sr_3B_2O_6:Ce^{3+}$ are also shown.

lauxetic effects originated from the dodecahedral activator center and the crystal structure of anticorundum,[14] respectively. A good evidence of absorption from activator ions is obtained through comparison of the DR spectra of host and activators doped $Sr_3B_2O_6$; on the other hand, high luminescent efficiency is expected in all samples because of the high reflectance in emissive regions, all observations are depicted in Fig. 1. Moreover, a conspicuous spectral overlap between the emission band of Ce^{3+} and the excitation band of Eu^{2+} was observed clearly in Figs. 1(a) and 1(b) and the effective resonance-type ET from a sensitizer Ce^{3+} to an activator Eu^{2+} ($ET_{Ce \rightarrow Eu}$) is expectable based on the significant spectral overlapping.

In this work the concentration of Ce^{3+} is fixed at the optimal doping level of 0.01 with varied Eu^{2+} codoping contents to investigate the energy transfer phenomenon. Figure 2(a) shows the PL spectra for $Sr_3B_2O_6:1\%Ce^{3+}, n\%Eu^{2+}$ phosphors with different n's of 0, 0.10, 0.15, 0.20, 0.25, and 0.70, which were measured at excitation wavelength of 351 nm, corresponding to the optimal excitation wavelength of the energy donor Ce^{3+}. With increasing Eu^{2+} content (n), the PL intensity of Eu^{2+} was observed to increase systematically from $n = 0.10$ to 0.15, and reach saturation as n equal to or larger than 0.2, whereas that

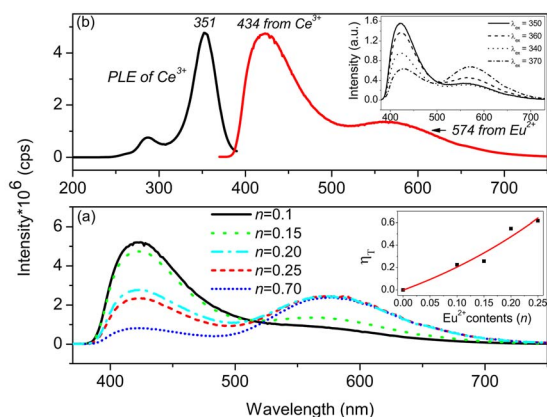of Ce^{3+} was simultaneously found to decrease gradually from $n = 0.10$ to 0.70. The observed saturation in Eu^{2+} intensity might be attributed to the results of other nonradiative relaxation present in the host matrix or $Eu^{2+}-Eu^{2+}$ internal concentration quenching effect. The above-described observations confirmed that the $ET_{Ce \rightarrow Eu}$ in SBO:Ce,Eu and the calculated $Ce^{3+} \rightarrow Eu^{2+}$ energy transfer efficiency (η_T) can be expressed by[15]

$$\eta_T = 1 - \frac{I_S}{I_{S0}},$$

where I_{S0} and I_S are the luminescence intensities of the sensitizer (Ce^{3+}) with and without activator (Eu^{2+}) present. The η_T of $Sr_3B_2O_6: 1\%Ce^{3+}, n\%Eu^{2+}$ was calculated as a function of n and represented in the inset of Fig. 2(a), in which η_T was found to increase gradually with increasing Eu^{2+} dopant content. Figure 2(b) portrays the detailed PLE/PL spectra for $Sr_3B_2O_6: 1\%Ce^{3+}, n\%Eu^{2+}$, where n is equal to 0.15. As indicated in Figs. 1(a) and 1(b), the PLE spectra for $Sr_3B_2O_6: 1\%Ce^{3+}, nEu^{2+}$ obtained by monitoring λ_{em} at 434 and 574 nm, respectively, are different. When the emission wavelength was monitored at 434 nm, we have found the PLE spectrum of $Sr_3B_2O_6: 1\%Ce^{3+}, n\%Eu^{2+}$ to be identical to that of solely Ce^{3+}-doped $Sr_3B_2O_6$; on the other hand, when the emission wavelength was monitored at 574 nm, the observed PLE spectrum resembles that of $Sr_3B_2O_6:Eu^{2+}$; however, two broad emission bands centering at 434 and 574 nm ascribed to the emission of Ce^{3+} and Eu^{2+}, respectively, are observed in PL spectrum. Furthermore, the conversion efficiency portrayed in PL spectra of the phosphor under UV excitations of 340, 350, 360, and 370 nm is also shown in the inset of Fig. 2(b). Actually, the conversion efficienies under the excitations of 360 and 370 nm are about 87% and 50%, respectively, of the optimal excitation wavelength (i.e., 351 nm), indicating that our phosphor is also effective under longer UV excitation.

Based on Dexter's energy transfer formula of multipolar interaction and Reisfeld's approximation, the following relation can be obtained:[15,16]

$$\frac{\eta_0}{\eta} \propto C^{a/3},$$

where η_0 and η are the luminescence quantum efficienies of Ce^{3+} in the absence and presence of Eu^{2+}, respectively; the values of η_0 / η can be approximately calculated by the ratio of related luminescence intensities (I_{S0}/I_S), C is the content of Eu^{2+}, and $a = 6$ and 8 correspond to dipole-dipole and dipole-quadrupole interactions, respectively. The I_{S0}/I_S-$C^{a/3}$ plots are further illustrated in Figs. 3(a) and 3(b), and the linear relationship were observed when $n = 6$ and 8. Electric dipole-dipole interaction with larger Columbic effect usually accompanies electric dipole-quadrupole interaction; therefore, the electric dipole-dipole interaction predominates in the ET mechanism from Ce^{3+} to Eu^{2+} in SBO:Ce,Eu, which is similar to the results of our previous study.[17]

For electric dipole-dipole interaction, the critical distance (R_c) of $ET_{Ce \rightarrow Eu}$ can be expressed by[16]

$$R_c^6 = 0.63 \times 10^{28} \frac{Q_A}{E^4} \int F_S(E)F_A(E)dE,$$

where $Q_A = 4.8 \times 10^{-16}$ f_d is the absorption cross section of Eu^{2+} ions, $f_d \approx 0.02$ is the electric dipole oscillator strength

FIG. 2. (Color online) (a) PL spectra for $Sr_3B_2O_6: 1\%Ce, n\%Eu$ phosphors excited at 351 nm. Inset: dependence of the energy transfer efficiency η_T on Eu^{2+} content n. (b) PL and PLE spectra for $Sr_3B_2O_6: 1\%Ce, n\%Eu$ ($n = 0.15$). Inset: the conversion efficiency under UV excitation.
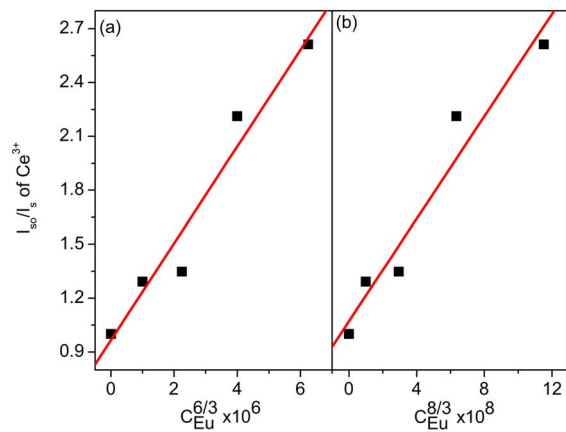
FIG. 3. (Color online) Dependence of I_{S0}/I_S of Ce^{3+} on (a) $C^{6/3}$ and (b) $C^{8/3}$.

FIG. 4. (Color online) CIE chromaticity diagram for $Sr_3B_2O_6$:$m\%$Ce,$n\%$Eu excited at 351 nm. (1) $m=1$, $n=0$; (2) $m=1$, $n=0.1$; (3) $m=1$, $n=0.15$; (4) $m=1$, $n=0.20$; (5) $m=1$, $n=0.25$; (6) $m=1$, $n=0.7$; and (7) $m=0$, $n=1$. The corresponding CIE chromaticity coordinates (x,y) are (1) (0.20, 0.16), (2) (0.25, 0.19), (3) (0.31, 0.24), (4) (0.43, 0.36), (5) (0.44, 0.37), (6) (0.49, 0.44), and (7) (0.53, 0.46). The Ce:YAG and GaN based white-emitting systems are compared with this work and portrayed in red line.

for Eu^{2+} ions, and $\int F_S(E)F_A(E)dE$ represents the spectral overlap between the normalized spectral shapes of Ce^{3+} emission $F_S(E)$ and Eu^{2+} excitation $F_A(E)$, and it is estimated to be about 1.13 eV^{-1}; E (in eV) is the maximum energy of spectral overlap. Therefore, the R_c of $ET_{Ce \rightarrow Eu}$ in SBO:Ce,Eu was calculated to be about 30.67 Å, which is slightly shorter than that (i.e., 32.7 Å) in Ba_2ZnS_3:Ce,Eu reported by our group.[17] When $Ce^{3+}-Eu^{2+}$ was supposed to form a close pair at a distance of 3.59 Å, which is the nearest distance between Sr and Sr sites, and, hence, R_c was approximated as 8.5 times of lattice dimension in length.

In many cases, concentration quenching is due to energy transfer from one activator to another until energy sink in the lattice is reached.[18] Blasse suggested that the critical distance (R_c) of energy transfer can be expressed by[16]

$$R_c \approx 2\left(\frac{3V}{4\pi x_c N}\right)^{1/3},$$

where V is the volume of the unit cell, x_c is the critical concentration, at which the luminescence intensity of sensitizer (Ce^{3+}) is half that in the sample in the absence of activator (Eu^{2+}), namely, x_c occurs when η_T equals 0.5, and N is the number of host cations in the unit cell. For $Sr_3B_2O_6$ host, V is 889.93 Å,[3] N is 18,[11] and x_c is 0.002 07 determined from the inset of Fig. 2(a). Therefore, the critical distance for energy transfer R_c is estimated to be about 35 Å, which agrees approximately with that obtained by using the spectral overlap method.

The CIE chromaticity coordinates with varied hues for SBO:Ce,Eu excited at 351 nm were measured and shown in Fig. 4. With increasing Eu^{2+} content, the color tone changes from blue, which is represented by point 1 (solely Ce^{3+} doped) through white (Ce^{3+}/Eu^{2+} coactivated) and finally to yellow, which is represented by point 7 (solely Eu^{2+} doped), corresponding to chromaticity coordinates (x,y) varying from (0.20, 0.16) to (0.31, 0.24) and ultimately to (0.53, 0.46). Hence, by properly tuning the ratio of Ce^{3+}/Eu^{2+}, the diversified white light with different hues can be achieved under UVLEDs radiation. Higher CRI values can be anticipated in our single-phased white phosphors because of more red-light component contribution from Eu^{2+} emission included than that of the commercial YAG:Ce based white-emitting system.

In conclusion, we have demonstrated that the energy transfer from Ce^{3+} to Eu^{2+} in $Sr_3B_2O_6$:Ce^{3+},Eu^{2+} is domi-
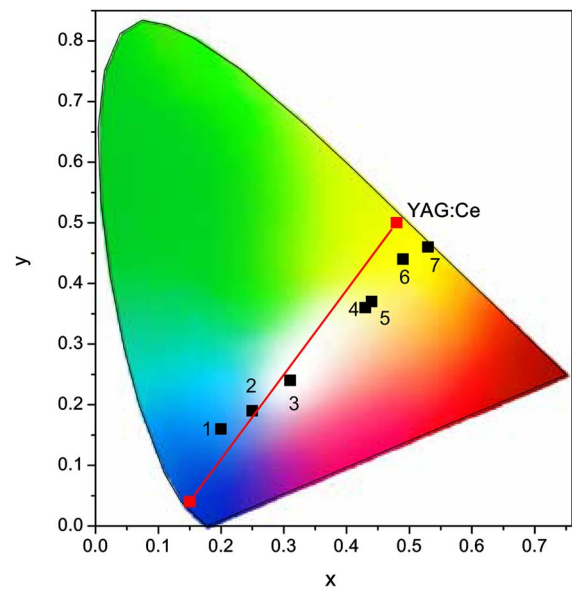
nated by resonance-type electric dipole-dipole interaction. In addition, the tunable color hues from blue through white and finally to yellow-orange is achieved by properly tuning the relative Ce^{3+}/Eu^{2+} ratio in $Sr_3B_2O_6$:Ce,Eu.

[1]Y. Shimizu, K. Sakano, Y. Noguchi, and T. Moriguchi, US Patent No. 5998925 (December 7, 1998).
[2]G. Blasse and B. C. Grabmaier, *Luminescent Materials* (Springer, Berlin, Germany, 1994), p. 46.
[3]J. S. Kim, P. E. Jeon, J. C. Choi, H. L. Park, S. I. Mho, and G. C. Kim, Appl. Phys. Lett. **84**, 2931 (2004).
[4]J. S. Kim, P. E. Jeon, Y. H. Park, J. C. Choi, H. L. Park, G. C. Kim, and T. W. Kim, Appl. Phys. Lett. **85**, 3696 (2004).
[5]J. S. Kim, K. T. Lim, Y. S. Jeong, P. E. Jeon, J. C. Choi, and H. L. Park, Solid State Commun. **135**, 21 (2005).
[6]W. J. Yang, L. Luo, T. M. Chen, and N. S. Wang, Chem. Mater. **17**, 3883 (2005).
[7]W. J. Yang and T. M. Chen, Appl. Phys. Lett. **88**, 101903 (2006).
[8]S. H. Lee, J. H. Park, S. M. Son, and J. S. Kim, Appl. Phys. Lett. **89**, 221916 (2006).
[9]J. S. Kim, A. K. Kwon, Y. H. Park, J. C. Choi, H. L. Park, and G. C. Kim, J. Lumin. **122-123**, 583 (2007).
[10]C. K. Chang and T. M. Chen, Appl. Phys. Lett. **90**, 161901 (2007).
[11]L. Richter and F. Muller, Z. Anorg. Allg. Chem. **467**, 123 (1980).
[12]W. J. Schipper, D. van der Voort, P. van den Berg, Z. A. E. P. Vroon, and G. Glasse, Mater. Chem. Phys. **33**, 311 (1993).
[13]G. Blasse and B. C. Grabmaier, *Luminescent Materials* (Springer, Berlin, Germany, 1994), p. 45.
[14]A. Vegas, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **41**, 1689 (1985).
[15]Y. Tan and C. Shi, J. Phys. Chem. Solids **60**, 1805 (1999).
[16]G. Blasse, Philips Res. Rep. **24**, 131 (1969).
[17]W. J. Yang and T. M. Chen, Appl. Phys. Lett. **90**, 171908 (2007).
[18]D. L. Dexter and J. A. Schulman, J. Chem. Phys. **22**, 1063 (1954).