

Synthesis and photoluminescence characteristics of color-tunable BaY₂ZnO₅:Eu³⁺ phosphors

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(Received 2 August 2008; accepted 17 September 2008; published online 25 November 2008)

Color-tunable phosphors of BaY_{2-x}Eu_xZnO₅ ($x=0.001-0.9$) were synthesized using a vibrating milled solid state reaction. The results indicate that the emission spectra of BaY_{2-x}Eu_xZnO₅ samples excited at 395 nm exhibit a series of shaped peaks assigned to the ${}^5D_0 \rightarrow {}^7F_J$ ($J=0,1,2,3,4$) transitions. Luminescence from the higher excited states, such as 5D_1 , 5D_2 , and 5D_3 , were also observed even though the Eu³⁺ concentration was up to $x=0.2$. The chromaticity coordinate of BaY_{2-x}Eu_xZnO₅ phosphors varies with the Eu³⁺-doped concentrations from blue, white, to red, and which may be potentially applicable as a white light emitting phosphor for ultraviolet light emitting diodes. © 2008 American Institute of Physics. [DOI: 10.1063/1.2998299]

White light emitting diodes (LEDs) are candidates for new lighting systems in the future. The most dominant white LED uses a 450–470 nm blue emitting diode that excites a yellow-emitting yttrium aluminum garnet (YAG):Ce³⁺ phosphor.¹ However, the light color is not true because this system lacks of a red emitting component.² Current lighting technology employs UV-LED with triple-wavelength RGB phosphors to improve this problems.³ Recently, a lot of attention has been given to single-phased white light emitting phosphors,^{4–7} which have a large potential for white light LED applications. A proper host material doped with various concentrations of Eu³⁺ phosphors can generate red emission from the 5D_0 level and the blue and green emissions from higher 5D levels, including 5D_1 , 5D_2 , and 5D_3 of Eu³⁺, which could produce single-phased white light emitting phosphors.

BaY₂ZnO₅ is a luminescence host with a stable crystal structure and high thermal stability. BaR₂ZnO₅ ($R^{3+} = \text{Eu}^{3+}, \text{Y}^{3+}$) has an orthorhombic structure with a space group of *Pbnm*.⁸ The basic structure of BaY₂ZnO₅ consists of YO₇, BaO₁₁, and ZnO₅ polyhedra. Y is sevenfold coordinated inside a monocapped trigonal prism. These prisms share edges to form wavelike chains parallel to the long *b*-axis, and two such units join to form the basic structure of Y₂O₁₁. R³⁺ ions occupy two different sevenfold oxygen-coordinated sites with the same site symmetry (*C_s*), but a slightly different R-O distance. A previous study identified two sites of Eu³⁺ ions with similar 4*f* energy level in BaEu₂ZnO₅.⁹ In the present study, the authors demonstrated single-phased white-emitting phosphors and a high color purity red phosphor in BaY₂ZnO₅:Eu³⁺ for near UV light excitation.

Specimens of Eu³⁺ ion doped BaY₂ZnO₅ were synthesized using a vibrating milled solid state reaction. The raw materials were BaCO₃, ZnO, Y₂O₃, and Eu₂O₃ with a purity of 99.99%. After they had been mechanically activated by grinding in a high energy vibromill for 15 min with zirconia balls in a polyethylene jar, the mixtures were calcined at 1250 °C for 12 h in air.

Figure 1 shows the excitation spectra of BaY_{1.98}Eu_{0.02}ZnO₅ phosphor in the UV region from 200 to 400 nm. The excitation spectra were monitored at an emission wavelength of 418 nm for ${}^5D_3 \rightarrow {}^7F_1$ transition [Fig. 1(a)], 472 nm for ${}^5D_2 \rightarrow {}^7F_1$ transition [Fig. 1(b)], 537 nm for ${}^5D_1 \rightarrow {}^7F_1$ transition [Fig. 1(c)], and 625 nm for ${}^5D_0 \rightarrow {}^7F_2$ transition [Fig. 1(d)]. The broadband centered at 284 nm is assigned to the charge transition state (CTS) from O²⁻ to Eu³⁺ ions of the host lattice. The sharp peaks from 320 to 410 nm are attributed to the intra-4*f* forbidden transitions of Eu³⁺. The strongest excitation line at 395 nm contributes to the ${}^7F_0 \rightarrow {}^5L_6$ transition in the near UV region. Additionally, Fig. 1 also indicates that higher energy states, such as ${}^5D_{3,2}$ transition, have a lower intensity of CTS to *f-f* transition ratio (CTS/*f-f* transition) than that of lower energy states, such as ${}^5D_{1,0}$ transition. Similar results were observed in other studies.¹⁰ This is due to CTS having a larger band offset than *f-f* transition¹¹ so CTS can feed directly to the lower energy states of ${}^5D_{1,0}$. In contrast to CTS, 4*f* electrons are well shielded from the surroundings by filled 5*s* and 5*p*¹² so the influence of the offset for *f-f* transition can be neglected. Therefore, ${}^5D_{1,0}$ state transition is more effective than ${}^5D_{3,2}$ transition under CTS excitation.

The emission spectra of BaY_{1.98}Eu_{0.02}ZnO₅ phosphor under excitations of 395 nm (*f-f* transition) and 284 nm (CTS) are illustrated in Fig. 2. The emission spectra show a completely different radiation between ${}^5D_{3,2}$ and ${}^5D_{1,0}$ transitions under excitation wavelengths of 395 and 284 nm. The intensities of the ${}^5D_{1,0}$ emission line are higher than those of other ${}^5D_{3,2}$ emission lines under an excitation wavelength of 284 nm. However, the opposite is true for an excitation wavelength of 395 nm. These results are in agreement with the behavior of the CTS band offset as discussed previously.

The emission behavior of BaY₂ZnO₅ doped with phosphor with various concentrations of Eu³⁺ ions under an excitation of 395 nm is illustrated in Fig. 3. The characteristic peak of Eu³⁺ ion intra-4*f* transitions from excited states to lower levels are 5D_3 (blue emission) $\rightarrow {}^7F_J$ ($J=1,2,3$) transition, 5D_2 (blue-green emission) $\rightarrow {}^7F_J$ ($J=0,1,2,3$), 5D_1 (green emission) $\rightarrow {}^7F_J$ ($J=1,2,3$), and 5D_0 (red emission) $\rightarrow {}^7F_J$ ($J=0,1,2,3,4$). The higher level

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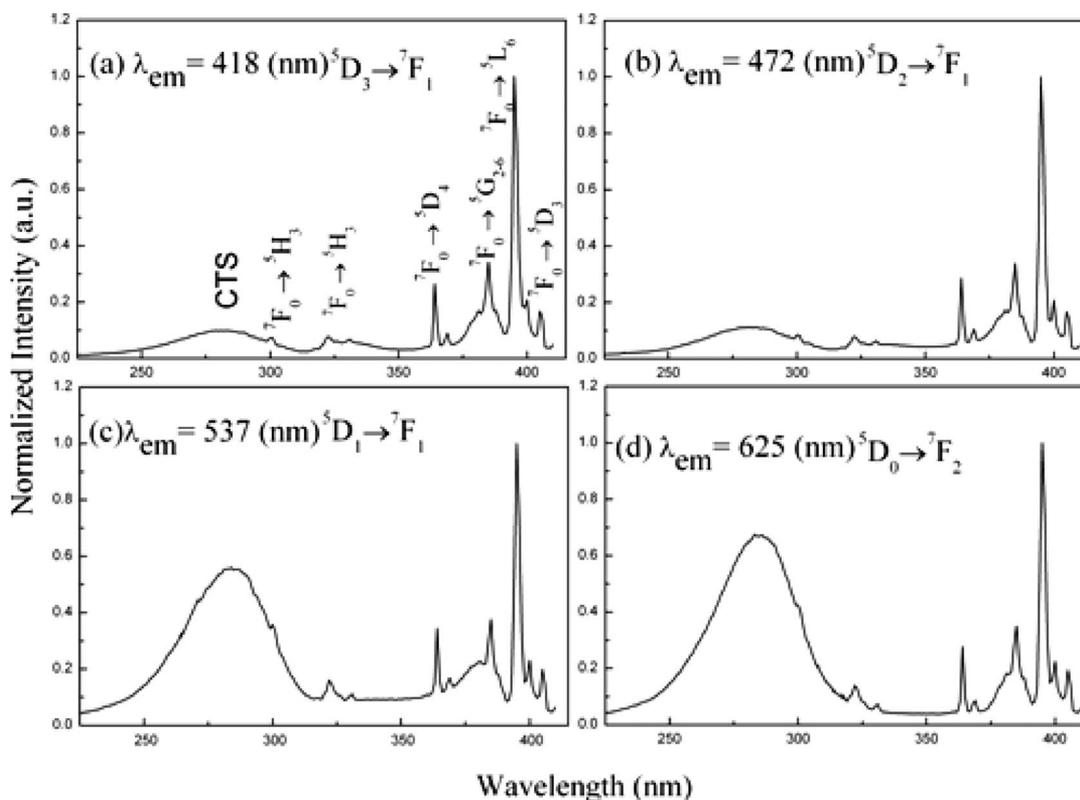


FIG. 1. Photoluminescence excitation spectra of $\text{BaY}_{1.98}\text{Eu}_{0.02}\text{ZnO}_5$ prepared at 1250 °C for 12 h monitored at emission wavelengths of (a) 418 nm, (b) 472 nm, (c) 537 nm, and (d) 625 nm.

5D_J ($J=1,2,3$) emission depends on the concentration of Eu^{3+} ions. The emission spectra show a completely different ratio between the $^5D_{3,2,1}$ blue-green emission and 5D_0 red emission for lower and higher Eu^{3+} concentrations. The dominant transition of $\text{BaY}_{2-3}\text{Eu}_x\text{ZnO}_5$ phosphors for lower Eu^{3+} ion concentrations are $^5D_3 \rightarrow ^7F_J$ (blue emission) and

$^5D_2 \rightarrow ^7F_J$ (blue-green emission). The intensities of the emission peaks from $^5D_{3,2}$ transition decrease with increasing Eu^{3+} concentration, and the intensities of the emission peaks from $^5D_{1,0} \rightarrow ^7F_J$ transition increase gradually. This result is due to concentration quenching by the cross-relaxation process.¹²

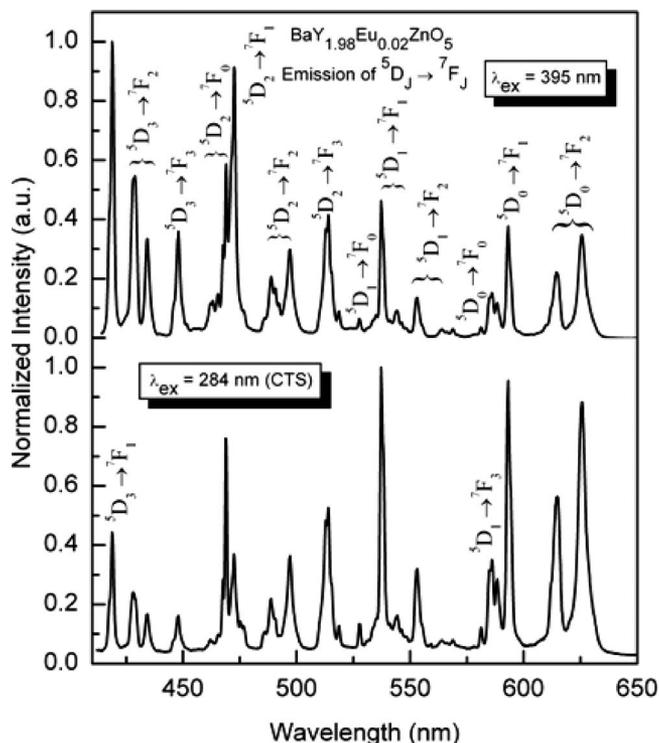


FIG. 2. Photoluminescence emission spectra of $\text{BaY}_{1.98}\text{Eu}_{0.02}\text{ZnO}_5$ prepared at 1250 °C for 12 h in air under excitations of 395 and 284 nm.

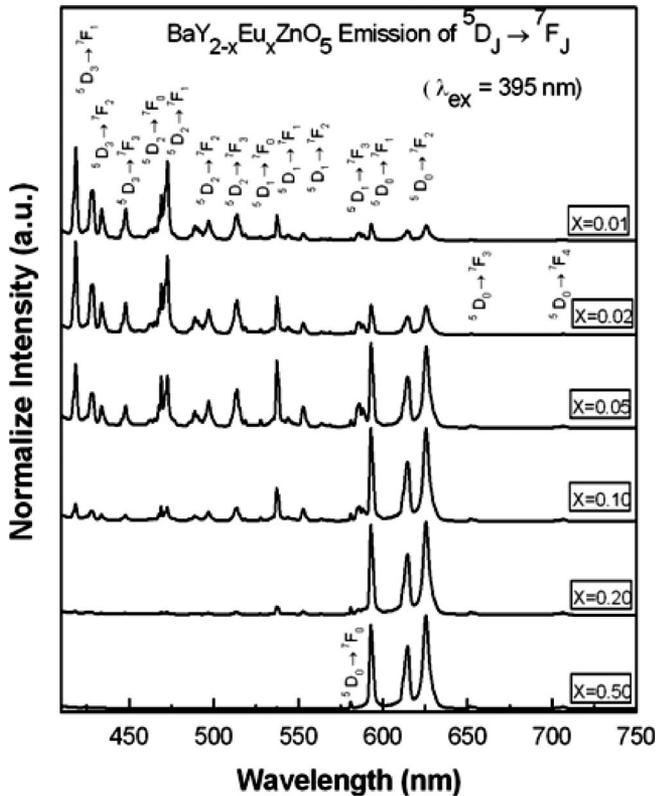


FIG. 3. Photoluminescence emission spectra of $\text{BaY}_{2-x}\text{Eu}_x\text{ZnO}_5$ doped with various amounts of Eu^{3+} calcined at 1250°C for 12 h in air.

In this nonradiative process, excitation energy from decaying ions forms a higher excited state ($^5D_{3,2,1}$) of Eu^{3+} ions, promoting neighboring ions from the ground state to a metastable state level, as $^5D_1(\text{Eu}_1) + ^7F_0(\text{Eu}_2) \rightarrow ^5D_0(\text{Eu}_1) + ^7F_3(\text{Eu}_2)$.¹² As a result, if the Eu^{3+} ion concentration is sufficiently high, the higher level emission can be easily quenched and the lower level emission becomes dominant. Finally, the $\text{BaY}_{2-x}\text{Eu}_x\text{ZnO}_5$ phosphor emits bright red luminescence when the Eu^{3+} ion concentration is $x \geq 0.3$. The dominant emission peaks at 593, 614, and 626 nm are attributed to the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ of the Eu^{3+} intra- $4f^6$ transition, respectively. For $\text{BaY}_{2-x}\text{Eu}_x\text{ZnO}_5$, the site symmetry of Eu^{3+} (Y^{3+}) is C_s , which lacks inversion symmetry. Therefore, the emission of the electric dipole transition ($^5D_0 \rightarrow ^7F_2$) of Eu^{3+} ions in this compound is more sensitive than that of magnetic dipole transition ($^5D_0 \rightarrow ^7F_1$).¹²

The Commission Internationale de l'Éclairage (CIE) chromaticity coordinates with various color tones for $\text{BaY}_{2-x}\text{Eu}_x\text{ZnO}_5$ phosphors excited at 395 nm are illustrated in Fig. 4. With increasing Eu^{3+} ion concentration, the color tone changes from blue (which is represented by points 1 and 2), through white (which is represented by points 4–7) and finally to red, which is represented by point 13 ($x=0.4$) located at (0.66, 0.34) and is very close to the standard red chromaticity (0.67, 0.33) for the National Television Standard Committee (NTSC) system. When Eu^{3+} ion concentration is larger than $x=0.4$, the Eu^{3+} emission color does not change. In particular, $\text{BaY}_{1.96}\text{Eu}_{0.04}\text{ZnO}_5$ phosphors show white light emission, which has CIE color coordinates $x=0.33$, $y=0.29$. For the reasons mentioned above, the emission color of $\text{BaY}_{2-x}\text{Eu}_x\text{ZnO}_5$ phosphors can be tuned by a

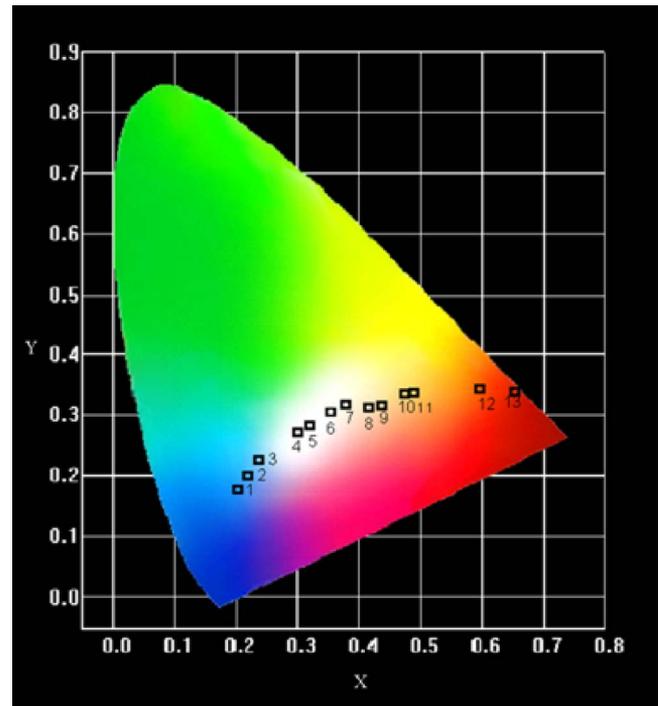


FIG. 4. (Color online) CIE color coordinate diagram of $\text{BaY}_{2-x}\text{Eu}_x\text{ZnO}_5$ phosphors. Data points 1–13 are assigned to Eu^{3+} concentrations of $x=0.005, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.2, 0.3$, respectively.

proper Eu^{3+} concentration without doping other color centers in a single-phased host lattice.

In summary, color-tunable $\text{BaY}_2\text{ZnO}_5:\text{Eu}^{3+}$ phosphors have been produced by adjusting the Eu^{3+} ion concentration. $\text{BaY}_{1.96}\text{Eu}_{0.04}\text{ZnO}_5$ phosphors are single phased and white emitting with a CIE chromaticity coordinate (x, y) of (0.33, 0.29). The optimal PL intensity of red emission is $x=0.4$. The red emission of the $\text{BaY}_{1.6}\text{Eu}_{0.4}\text{ZnO}_5$ phosphor has CIE chromaticity coordinates of (0.66, 0.34), which is very close to the NTSC system standard red chromaticity (0.67, 0.33).

The authors would like to thank the National Science Council of Taiwan, Republic of China, for financially supporting this research under Contract No. NSC96-2622-E-150-034-CC3.

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