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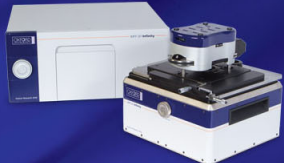
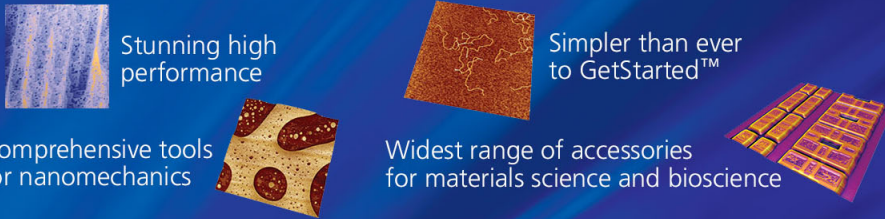
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Ce³⁺/Eu²⁺ codoped Ba₂ZnS₃: A blue radiation-converting phosphor for white light-emitting diodes

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The Ce³⁺/Eu²⁺ codoped Ba₂ZnS₃ phosphor shows intense blue absorption and tunable green-to-red emission. The energy transfer from Ce³⁺ to Eu²⁺ in this phosphor has been demonstrated to be a resonant type via an electric dipole-dipole mechanism. The Ba₂ZnS₃:Ce³⁺,Eu²⁺ phosphor would be the great potential application as a blue radiation-converting phosphor for white light-emitting diodes. © 2007 American Institute of Physics. [DOI: 10.1063/1.2731685]

White light-emitting diodes (LEDs) could be produced by blue chip-pumped yellow Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce),¹ whereas color rendering index (CRI) of white light made by the complementary blue and yellow emission is deficient due to the lack of red light contribution. Hence, several red phosphors were developed to add into the above-mentioned system in order to improve CRI.^{2–6} Unfortunately, the extreme difference in degradation between different host phosphors will produce color aberration. Accordingly, it is important to investigate a single-host phosphor with green-to-red emission bands for blue LEDs. A phosphor could emit a couple of radiation by codoping activators with *f-d* or *d-d* electron configurations,⁷ such as Eu²⁺/Mn²⁺,^{8–11} Ce³⁺/Mn²⁺,^{12,13} and Ce³⁺/Eu²⁺,^{13–16} the energy transfer (ET) would occur between activator/coactivator couples by effective resonant type via a multipolar interaction and the ET to Mn²⁺ can be of exchange interaction.^{8–16} Nevertheless, in the past few years, coactivated single-host phosphors with blue absorption or for blue LEDs were rarely investigated. In this work, we have explored and discovered a single-host phosphor, Ce³⁺/Eu²⁺ codoped Ba₂ZnS₃, which shows ultraviolet-to-blue absorption and green-to-red emission, exhibiting great potential application in white LEDs while a blue chip is coupled.

Ba₂ZnS₃ was prepared and reported in 1959 by Hoppe,¹⁷ until 1961, its crystal structure was determined by Schnerung *et al.*;¹⁸ the luminescence of Ba₂ZnS₃:Ce³⁺ was reported by Lin *et al.*¹⁹ Nonetheless, the luminescence properties of Ce³⁺/Eu²⁺ codoped Ba₂ZnS₃ were not reported in literatures. Therefore, we report herein the investigation of the luminescence properties and ET phenomenon between activators and demonstrate that white light emission can be achieved in Ba₂ZnS₃:Ce³⁺,Eu²⁺ (BZS:Ce,Eu).

Ba₂ZnS₃ has two crystallographically independent cation sites in a unit cell: a seven-coordinated Ba²⁺ site and a four-coordinated Zn²⁺ site.¹⁸ We could propose that Ce³⁺ and Eu²⁺ are both expected to occupy the Ba²⁺ sites preferably because the ionic radii of Ce³⁺ (1.07 Å) and Eu²⁺ (1.20 Å) are close to that of Ba²⁺ (1.38 Å).²⁰ However, the Zn²⁺ sites (0.60 Å) are too small for Ce³⁺ and Eu²⁺ to occupy.²⁰

The absorption spectrum of Ba₂ZnS₃ host reveals a direct band gap of about 3.3 eV, as shown in Fig. 1; the pho-

toluminescence (PL) spectrum of that shows an emission band centered at 623 nm. As presented in Fig. 2, the photoluminescence excitation (PLE) spectrum of Ba₂ZnS₃:Ce³⁺ shows two excitation bands centered at 364 and 420 nm, assigned to host-lattice absorption and 4*f*¹ → 5*d*¹ transition of Ce³⁺, respectively. In addition, as expected the PLE intensity ratio (*I*_{364 nm}/*I*_{420 nm}) of that is found to decrease as the Ce³⁺ concentration increases, indicating that Ce³⁺ ions undoubtedly substitute for Ba²⁺ sites. The PL spectrum of Ba₂ZnS₃:Ce³⁺ shows an asymmetric band emission deconvoluted into two peaks centered at 489 and 540 nm, attributed to the transitions from 5*d*¹ to ²F_{5/2} and ²F_{7/2}, respectively. The spin-orbit splitting of ground state (²F_J) for Ce³⁺ was estimated at about 1900 cm⁻¹, approximating to that reported in Ref. 7. As depicted in Fig. 3, the PLE spectrum of Ba₂ZnS₃:Eu²⁺ shows a host-lattice absorption centered at 357 nm and an unresolved band from 375 to 570 nm assigned to the 4*f*⁶5*d*¹ multiplets of Eu²⁺ excited states; the PL spectrum of that displays a broad band deconvoluted into two peaks centered at 623 and 671 nm, attributed to host-lattice emission and 4*f*⁶5*d*¹ → 4*f*⁷(⁸S_{7/2}) transition of Eu²⁺, respectively. Moreover, the host-lattice emission still retains under 420 nm excitation because the conduction band edge of host lattice is close to the lowest energy level of Eu²⁺ excited state; at higher Eu²⁺ concentrations, the emission band does not show obvious change because the emission intensity of host lattice and Eu²⁺ decreases simultaneously under the influence of substitution of Eu²⁺ for Ba²⁺ and con-

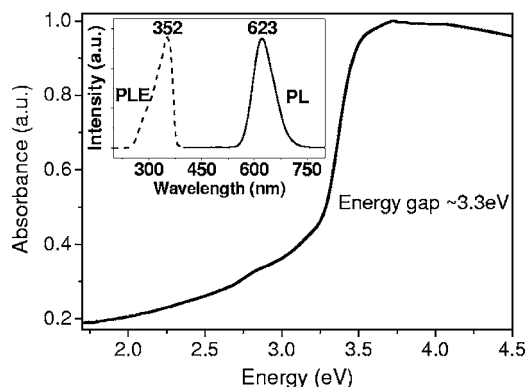


FIG. 1. Absorption spectrum of Ba₂ZnS₃ host; the inset for PLE and PL spectra of Ba₂ZnS₃ host (PLE monitored at 623 nm and PL excited at 352 nm).

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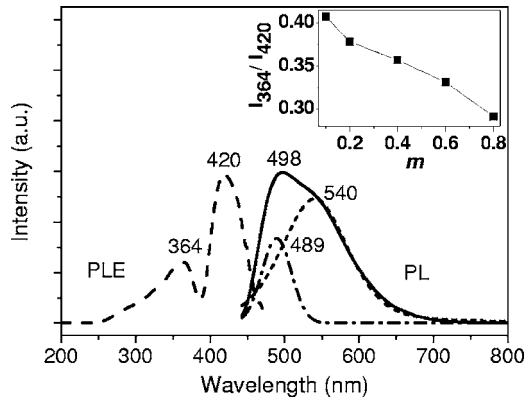


FIG. 2. PLE and PL spectra of $\text{Ba}_2\text{ZnS}_3:0.1\% \text{Ce}^{3+}$ (PLE monitored at 498 nm and PL excited at 420 nm); the inset for dependence of intensity ratio $I_{364 \text{ nm}}/I_{420 \text{ nm}}$ in $\text{Ba}_2\text{ZnS}_3:m\% \text{Ce}^{3+}$ on m .

centration quenching, respectively. In fact, the red emission of Eu^{2+} is the effect of the larger crystal-field splitting and the lower energy of the center of gravity of $5d$ level. The Stokes shift of Eu^{2+} was roughly calculated to be about 7800 cm^{-1} , and the large shift might be the result of the lower lattice stiffness.⁷ Besides, a significant spectral overlap was observed between the emission band of Ce^{3+} and the excitation band of Eu^{2+} exhibited in Fig. 4(a), with the result that the effective resonance-type ET from Ce^{3+} to Eu^{2+} is expected. Consequently, Ce^{3+} and Eu^{2+} are regarded as energy donor and energy acceptor, respectively.

The ET evidence from Ce^{3+} to Eu^{2+} excited at 420 nm is shown in Fig. 4(b); the red-emission intensity of $\text{Ce}^{3+}/\text{Eu}^{2+}$ codoped Ba_2ZnS_3 is higher than that of Eu^{2+} doped one. Furthermore, with increasing Eu^{2+} concentration, the PL intensity of Ce^{3+} as well as the total intensity of BZS:Ce,Eu are found to decrease gradually as displayed in Fig. 5. The ET efficiency (η_T) from Ce^{3+} to Eu^{2+} can be expressed by¹²

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

where I_{S0} and I_S are the luminescence intensity of Ce^{3+} in the absence and presence of Eu^{2+} , respectively. As Eu^{2+} content increases, the η_T is found to increase and finally saturate. Based on Dexter's ET formula of multipolar interaction and Reisfeld's approximation, the following relation can be obtained.²¹

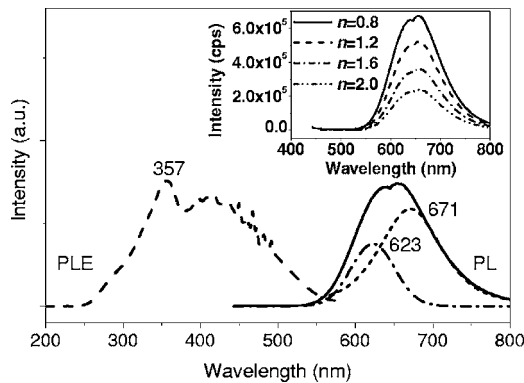


FIG. 3. PLE and PL spectra of $\text{Ba}_2\text{ZnS}_3:0.8\% \text{Eu}^{2+}$ (PLE monitored at 655 nm and PL excited at 357 nm); the inset for PL spectra of $\text{Ba}_2\text{ZnS}_3:n\% \text{Eu}^{2+}$ excited at 420 nm.

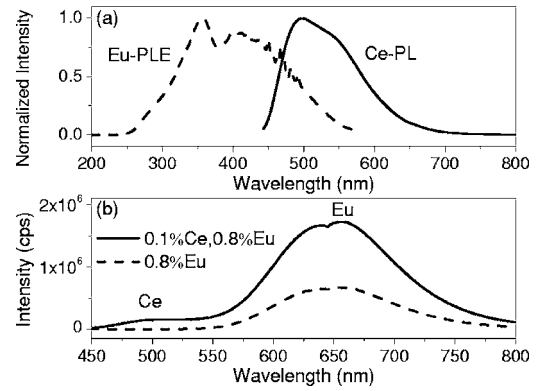


FIG. 4. (a) Spectral overlap between PLE spectrum of $\text{Ba}_2\text{ZnS}_3:\text{Eu}^{2+}$ (dashed line) and the PL spectrum of $\text{Ba}_2\text{ZnS}_3:\text{Ce}^{3+}$ (solid line); (b) PL spectra for $\text{Ba}_2\text{ZnS}_3:0.8\% \text{Eu}^{2+}$ and $\text{Ba}_2\text{ZnS}_3:0.1\% \text{Ce}^{3+}, 0.8\% \text{Eu}^{2+}$ excited at 420 nm.

$$\frac{I_{S0}}{I_S} \propto C^{\alpha/3}, \quad (2)$$

where C is the content of Eu^{2+} and $\alpha=6$ and 8 corresponding to electric dipole-dipole and dipole-quadrupole interactions, respectively. The plots represented in Figs. 6(a) and 6(b) both exhibit linear relationships; moreover, electric dipole-dipole interaction usually accompanies electric dipole-quadrupole interaction because the Coulombic effect of the former is larger than that of the latter. Therefore, the electric dipole-dipole interaction is dominant in the ET mechanism from Ce^{3+} to Eu^{2+} in BZS:Ce,Eu, which is similar to that observed in several references.¹³⁻¹⁶

For electric dipole-dipole mechanism, the critical distance (R_c) of ET from Ce^{3+} to Eu^{2+} can be expressed by²²

$$R_c^6 = 0.63 \times 10^{28} \frac{Q_A}{E^4} \int F_S(E)F_A(E)dE, \quad (3)$$

where $Q_A=4.8 \times 10^{-16} f_d$ is the absorption cross section of Eu^{2+} , $f_d \approx 0.02$ is the electric dipole oscillator strength for Eu^{2+} , $\int F_S(E)F_A(E)dE$ represents the spectral overlap between the normalized shapes of Ce^{3+} emission $F_S(E)$ and Eu^{2+} excitation $F_A(E)$, estimated at about 0.96 eV^{-1} , and E (in eV) is the maximum energy of spectral overlap. Therefore, the R_c of ET was calculated to be about 32.7 \AA , which is longer than that (25 \AA) reported in $\text{BaLiF}_3:\text{Ce},\text{Eu}$ because the spectral overlap (0.96 eV^{-1}) in BZS:Ce,Eu is larger than

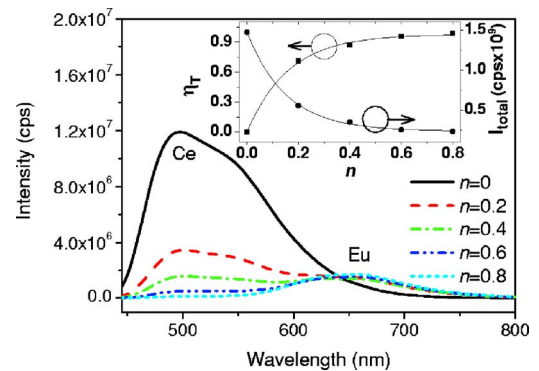


FIG. 5. PL spectra for $\text{Ba}_2\text{ZnS}_3:0.1\% \text{Ce}^{3+}, n\% \text{Eu}^{2+}$ excited at 420 nm; the inset showing dependence of η_T and total intensity in $\text{Ba}_2\text{ZnS}_3:0.1\% \text{Ce}^{3+}, n\% \text{Eu}^{2+}$ on n .

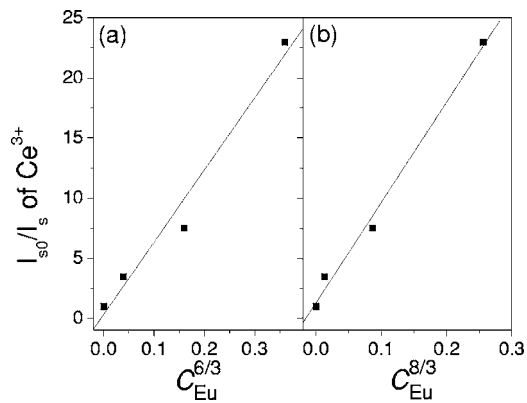


FIG. 6. Dependence of I_{50}/I_5 of Ce^{3+} on (a) $C^{6/3}$ and (b) $C^{8/3}$.

that (0.77 eV^{-1}) in $BaLiF_3:Ce,Eu$.¹⁴ When $Ce^{3+}-Eu^{2+}$ was supposed to form a close pair at a distance of 4.210 \AA , the shortest distribution length between Ce^{3+} and Eu^{2+} , the R_c of ET was approximated about eight lattice sites.

Because a commercial blue chip providing 420 nm was unavailable, the samples for blue LED application were simulated by measuring with a Xe light source with the same excitation wavelength. The Commission International de l'Eclairage (CIE) chromaticity coordinates for $BZS:Ce,Eu$ excited at 420 nm were also measured, and the results are shown in Fig. 7. The CIE chromaticity coordinates of Ce^{3+} - and Eu^{2+} -activated Ba_2ZnS_3 are $(0.34, 0.49)$ and $(0.64, 0.33)$, respectively, corresponding to hues of green-yellow and red. Furthermore, with increasing Eu^{2+} content, we have observed that the hues of $BZS:Ce,Eu$ locate in the yellow to

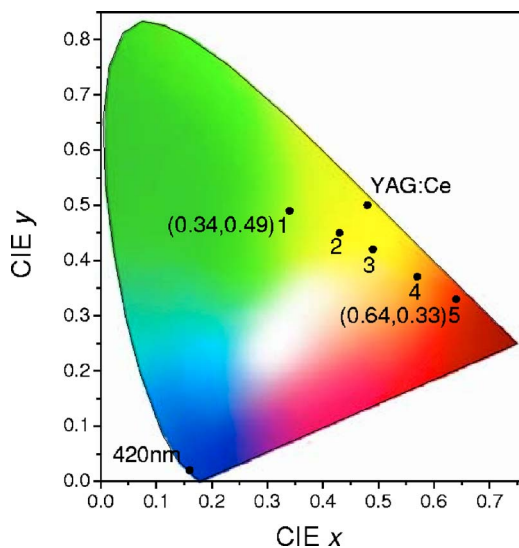


FIG. 7. CIE chromaticity diagram for $Ba_2ZnS_3:m\%Ce^{3+},n\%Eu^{2+}$ excited at 420 nm . (1) $m=0.1, n=0$; (2) $m=0.1, n=0.2$; (3) $m=0.1, n=0.4$; (4) $m=0.1, n=0.6$; and (5) $m=0, n=0.8$.

orange range. As a consequence, the tunable emission of $BZS:Ce,Eu$ coupled with blue LEDs could generate various white lights, which are more numerous than single-emitting $YAG:Ce$ coupled with ones. In addition, the CRI of white light generated by $BZS:Ce,Eu$ would be higher than that produced by $YAG:Ce$ because the former contains the red light component. Indeed, $BZS:Ce,Eu$ has the promising application for white LEDs.

In conclusion, the unprecedented $Ba_2ZnS_3:Ce^{3+},Eu^{2+}$ shows intense blue absorption and two emission bands: the one at 498 nm is attributed to Ce^{3+} , and the other at 655 nm is assigned to host lattice and Eu^{2+} . We have demonstrated that the energy transfer from Ce^{3+} to Eu^{2+} is of a resonant type via an electric dipole-dipole mechanism. All in all, $Ba_2ZnS_3:Ce^{3+},Eu^{2+}$ has been proven to be potentially useful as a blue radiation-converting phosphor for white light-emitting diodes.

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