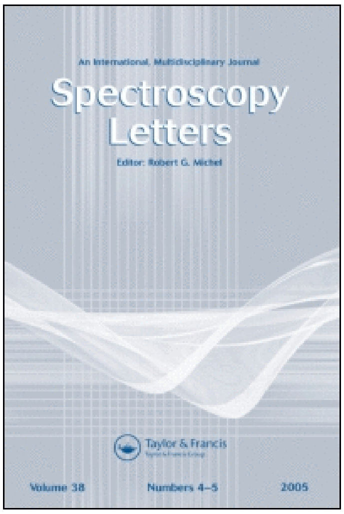

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Enhancement of Eu^{2+} Luminescence in BaO-SiO_2 Compounds Through Composition Modification

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Enhancement of Eu^{2+} Luminescence in BaO-SiO_2 Compounds Through Composition Modification

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ABSTRACT Phosphors of Eu^{2+}-doped BaO-SiO_2 compounds composed of a major $BaSiO_3$ phase and a minor Ba_2SiO_4 phase were synthesized by a solid-state method at 1200°C under CO atmosphere. An enhancement of the photoluminescence of Eu^{2+} up to 18 times has been achieved by mixing ZnO into the composition. The composition-optimized phosphor emits bright yellow–green luminescence with excitation between 380 and 420 nm, indicating potential of application in AlGaN-based UV-LEDs. Under the similar synthesis and measurement conditions, the emission band of the optimized phosphor is more intense and has stronger red component than that of Ba_2SiO_4:Eu^{2+}. Our experimental results suggest that the addition of ZnO may retain and stabilize Eu^{2+} in $BaSiO_3$ crystalline lattice and thus may enhance the 5d-4f luminescence and eliminate Eu^{3+} 4f-4f transition.

KEYWORDS luminescence enhancement, phosphors, silicates, white LEDs

INTRODUCTION

Conversion of blue emission from GaN light-emitting diode (LED) into white light by yellow phosphor YAG:Ce is one of the primary technologies for current commercial solid-state white-light devices. However, this type of white LED has rather low color-rendering index due to deficiency of red component in the emission spectra of Ce-activated garnets.[1–4] Invention of AlGaN LED with band edge in near-UV region between 380 and 400 nm provides an alternative route to obtain white LED for solid-state lighting through mixing phosphors of three base colors. A series of rare earth and transition metal ions–doped inorganic phosphors has been identified for application in UV LEDs.[5–7] However, the efficiency of the current UV-excited white LEDs does not satisfy the requirements of general lighting due to the internal low efficiency of AlGaN semiconductor, large Stokes losses from conversion of UV light into visible light in the region from blue to red, and the low luminescent efficiency of the identified phosphors. Therefore, significant improvement of luminescent efficiency of the phosphors with strong absorption bands in near-UV region is one of the key technologies for high efficient white LEDs.

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Silicates are widely used as phosphor hosts due to their abilities to incorporate rare-earth and transition-metal ions as luminescent centers, high thermal stability, high energy efficiency of the silicate phosphors, easy fabrication, and wide availability of inexpensive raw materials. Recently, a series of Eu^{2+} and Mn^{2+}-activated silicate phosphors has been studied for application in UV LEDs.[8–10] Among them, excited by UV LEDs, the phosphor of $Ba_3MgSi_2O_8$:Eu^{2+}, Mn^{2+} shows white light with color-rendering index higher than 85%, indicating its promise to exceed the current white LEDs fabricated with phosphor YAG:Ce and blue LEDs.

Although, phosphor Ba_2SiO_4:Eu^{2+} with a broad emission in green region has been extensively investigated for various applications.[11–13] However, there has been no further investigation on the luminescence properties of $BaSiO_3$:Eu^{2+} after studies reported 10 years ago by Blasse and coworkers.[14,15] It has been mentioned that $BaSiO_3$:Eu^{2+} shows broad yellow luminescence band with a maximum at 550 nm and 4.2 K. We chose this phosphor for more detailed studies on composition-property correlation because of its potential of application in white LEDs. As demonstrated in previous studies,[16–24] composition modification is a quite effective method to improve luminescence efficiency of lanthanide and transition metal ions in some inorganic materials. However, the mechanisms of such composition modifications are quite complicated and their explanations are generally based on assumptions and hypothesis according to limited experimental results and established theories such as charge compensation, creating new traps, and change of structure defects. More work is needed for a thorough understanding of composition modification–induced enhancement of luminescent efficiency for optimizing the identified phosphors and exploring more-novel phosphors. In the present work, a series of Eu^{2+}-doped phosphors in BaO-SiO_2 has been synthesized, and their luminescent properties have been investigated. A significant enhancement of Eu^{2+} luminescence is achieved by mixing ZnO into the composition. Several possible mechanisms responsible for the enhancement of luminescent efficiency are discussed.

MATERIALS AND METHODS

The luminescent materials studied in the present work were synthesized by a solid-state chemistry method. Starting materials of BaO, ZnO, SiO_2, and Eu_2O_3 with a ratio at 1BaO: x ZnO: 1 SiO_2: yEu_2O_3 ($x = 0$, 0.25, 0.5, 1.0, 1.5, 2.0; $y = 0.25\%$, 0.5%, 2%, 4%, 6%) were mixed homogeneously by continuous milling and sintered at 800°C for 12 hr in air and followed at 1200°C for 5 hr under the atmosphere produced by heated active carbon. Repeated grindings were performed between two sintering processes.

X-ray diffraction (XRD) measurements were performed on an X-ray diffractometer (Bruker D8) operated on Cu-Kα radiation. For luminescence measurement, a xenon lamp dispersed by a (SPEX 1704) monochromator was used as the excitation source, and the luminescence was detected by a cooled photomultiplier and lock-in amplifier. The measurements of luminescence at lower temperatures were performed with samples in a liquid helium cryostat. For decay time measurements, a pulsed (5 ns) Nd-YAG laser at 355 nm was used to pump the samples, and a digital oscilloscope was used to record the decay curves.

RESULTS AND DISCUSSION

Composition and Crystalline Structure

The crystal phase and structure of the synthesized samples in the BaO-SiO_2 series have been analyzed by XRD as shown in Fig. 1. A pure phase of Ba_2SiO_4 with orthorhombic structure and space group Pnam is obtained when the ratio of the starting materials BaO and SiO_2 is kept at 2:1. When the ratio of BaO and SiO_2 is fixed at 1, we cannot obtain a pure phase of $BaSiO_3$ but instead obtain a mixture of two phases, Ba_2SiO_4 and $BaSiO_3$. The $BaSiO_3$ phase has orthorhombic structure with space group P212121. With ZnO addition, the diffraction peaks attributed to Ba_2SiO_4 decrease, and the phase of $BaSiO_3$ dominates. A new phase of $Ba_2ZnSi_2O_7$ presents when the amount of ZnO increases to higher than 50 mol% of BaO. This new phase grows with increase of ZnO. However, a pure phase of $Ba_2ZnSi_2O_7$ could not be obtained with starting composition of BaO, ZnO, and SiO_2 at a ratio of 2:1:2 sintered at 1200°C for 5 hr. We believe that some interstitial crystallites containing Zn^{2+} may exist but are not formed as isolated phases that are detectable by XRD. Substituting Ba^{2+} ions with these interstitial Zn^{2+} ions is possible because Zn^{2+} ($r = 0.74$) is much smaller than Ba^{2+} ($r = 1.42$ A). The green–yellow luminescence is

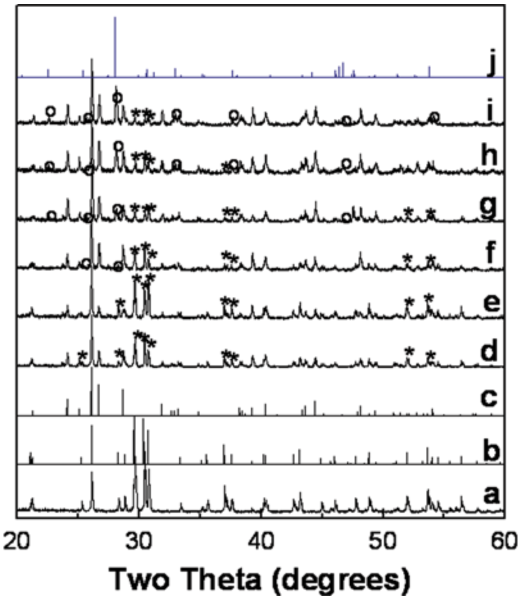

FIGURE 1 XRD patterns of BaO-SiO$_2$-ZnO system. Starting materials are at ratio of (a) 2BaO:SiO$_2$; and BaO:SiO$_2$ with addition of (d) 0 mol%, (e) 25 mol%, (f) 50 mol%, (g) 100 mol%, (h) 150 mol%, (i) 200 mol% ZnO of BaO. Curves (b), (c), and (j) are JCPD data of Ba$_2$SiO$_4$ (#26-1403), BaSiO$_3$ (#26-1402), Ba$_2$ZnSi$_2$O$_7$ (#23-0842) respectively. The empty spheres and stars mark the peaks of the Ba$_2$ZnSi$_2$O$_7$ and Ba$_2$SiO$_4$ phases respectively.

obviously from Eu^{2+} ions at the Ba^{2+} sites where charge compensation is not needed.

Figure 2 illustrates the crystal structures of BaSiO$_3$ and Ba$_2$SiO$_4$ referred to by the Cambridge Crystallographic Data Center. In these two structures, the Si^{4+} ions are located at the center of a tetrahedron coordinated with four O^{2-} ions. In BaSiO$_3$, the [SiO$_4$]$^{2-}$ tetrahedrons form a chain running parallel to *c* axis by sharing corners. The Ba^{2+} ions are accommodated in the tunnels between chains. Ba$_2$SiO$_4$ has zero-dimension structure, in which [SiO$_4$]$^{2-}$ tetrahedrons are structurally isolated from each other.

Enhancement of Photoluminescence

The enhancement of photoluminescence from Eu^{2+}-activated phosphor of the BaO-SiO$_2$ system is achieved by adding ZnO into the composition. In the phase-mixed system of BaO-SiO$_2$-ZnO (BSZ) doped with Eu^{2+} ions, the broad emission band in the green–yellow region is attributed to the parity-allowed 4f^{6}5d-to-4f^7 electronic transition of Eu^{2+}. As illustrated in Fig. 3, the integrated luminescence intensity increases up to 18 times by mixing ZnO into the BaO-SiO$_2$ system. Although the intensity increases significantly, only a slight red shift is observed in the luminescence spectra, which suggests that the crystallographic environment of Eu^{2+} undergoes no significant change induced by adding ZnO. In Fig. 4, broad absorption band from 320 to 440 nm and the efficient luminescence produced with excitation in the region of 380–420 nm indicate that the Eu^{2+}-doped BSZ phosphor has a potential for application in AlGaN-based UV-LEDs for solid-state lighting.

For evaluation of the luminescence efficiency of Eu^{2+}-doped BSZ (BSZ:Eu), a phosphor of pure Ba$_2$SiO$_4$:Eu^{2+} has been synthesized, and its emission spectra have been measured under the similar experimental conditions as those of BSZ:Eu. In comparison with the luminescence of Ba$_2$SiO$_4$:Eu^{2+}, as shown in Fig. 5, the emission bands of BSZ:Eu, measured both at 78 K (Fig. 5 Inset) and 298 K, are more intense and broader than those of Ba$_2$SiO$_4$:Eu^{2+}. Under radiation of a 366-nm excitation, Ba$_2$SiO$_4$:Eu^{2+} emits green light, while BSZ:Eu emits stronger green–yellow light

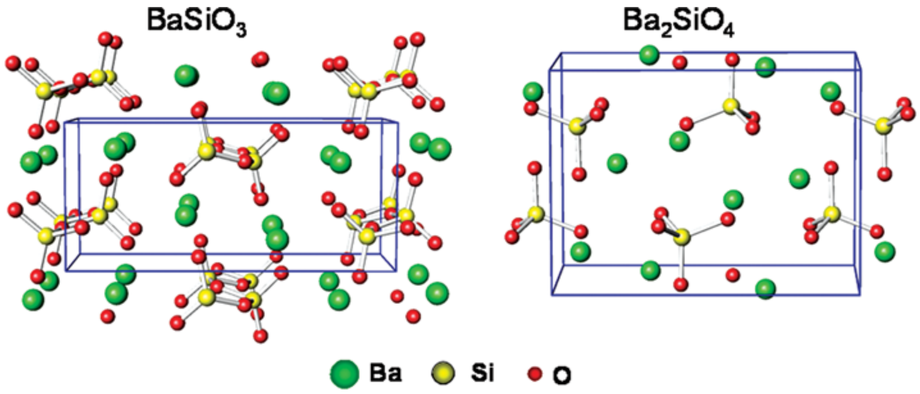

FIGURE 2 View of the chain structure of BaSiO$_3$ and zero-dimension structure of Ba$_2$SiO$_4$ referred to the Cambridge Crystallographic Data Center.

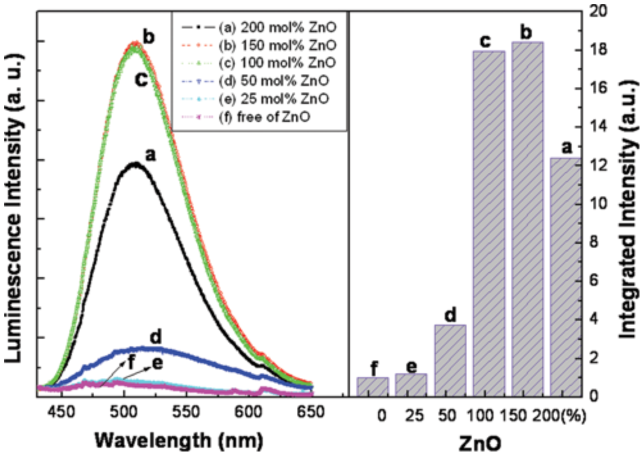

FIGURE 3 Enhancement of Eu^{2+} photoluminescence (excitation at 380 nm) in the BaO-SiO_2 system (with starting materials at molar ratio of BaO:SiO_2) induced by adding various amount of ZnO (a to e) in comparison with a sample without ZnO (f).

as its emission band extending to the longer wavelength region. It was previously reported that Eu^{2+} in the chain structure of $BaSiO_3$ experiences positive charges due to cation neighbors in the chain direction, in addition to the negative charges of the nearest anion neighbors.[11] The positive charges can orient on d-orbital preferentially, and a d-orbital will be more delocalized than those without a preferential orientation. As a result, the Stokes shift of Eu^{2+} emission will also be larger in $BaSiO_3$ than that in the zero-dimension structure of Ba_2SiO_4.

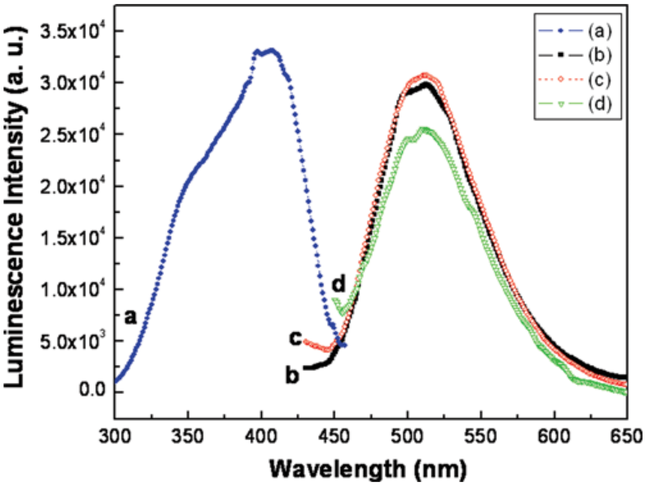

FIGURE 4 Excitation spectra monitored at 510 nm (a), and photoluminescence spectra of Eu^{2+}-doped BaO-SiO_2 system mixed with 100-mol% ZnO of BaO excited by a Xe lamp at 380 nm (b), 400 nm (c), and 420 nm (d).

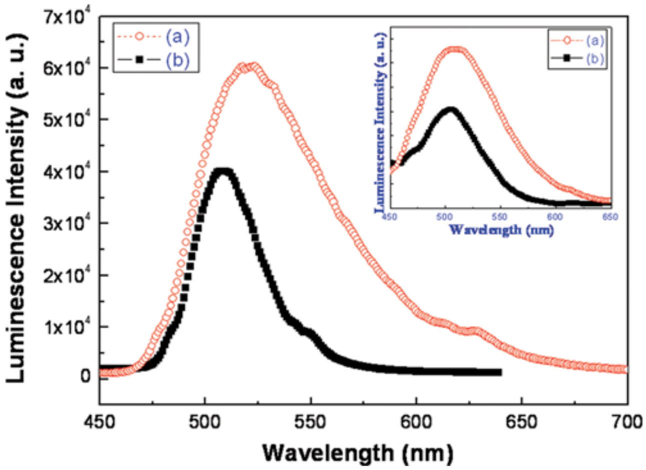

FIGURE 5 Photoluminescence of (a) Eu^{2+}-doped BaO-SiO_2 system mixed with 100-mol% ZnO of BaO, (b) Ba_2SiO_4:Eu^{2+} prepared at 1200°C for 5 hr in CO atmosphere and measured at 78 K (inset) and 298 K ($\lambda ex = 380$ nm).

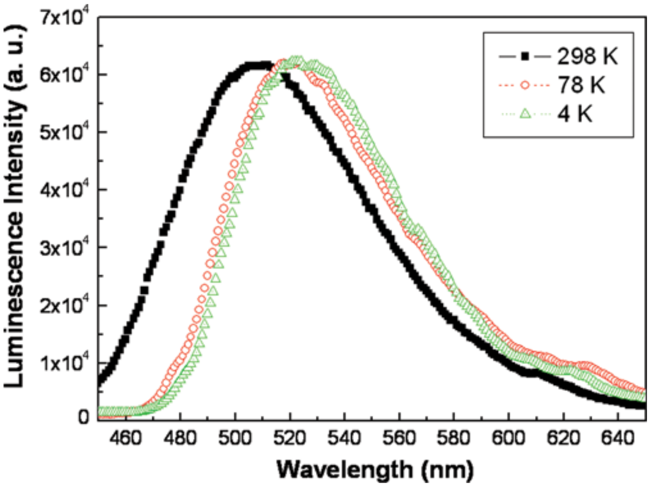

FIGURE 6 Photoluminescence of Eu^{2+}-doped BaO-SiO_2 system mixed with 100-mol% ZnO of BaO measured at different temperatures.

The normalized emission spectra of BZS:Eu^{2+} measured at 298 K, 78 K, and 4 K are shown in Fig. 6. The full width at half maximum decreases slightly with decreasing temperature, which is due to the relatively low population density of the phonon states at low temperatures. Evident red shift from 508 nm and 521 nm to 525 nm occurs when the temperature decreases from 298 K and 75 K to 4 K. According to the energy level structure of Eu^{2+} reported previously, this red shift is consistent with thermal population of the upper level excited states and the associated vibronic transitions.[12]

Mechanism of Eu^{2+} Photoluminescence Enhancement

Our experimental results indicate that the photoluminescence of Eu^{2+} in the BaO-SiO_2 system can be enhanced up to 18 times by mixing ZnO into the phosphor composition. In addition to luminescence intensity enhancement, there are other effects observed with the increase of ZnO addition, which provide important information on the consequence of the composition modification. As demonstrated in Fig. 7, in comparison with the sample without ZnO, a red shift of emission has also been observed in the sample with 100-mol% ZnO addition, which is due to the decrease of the ratio of Ba_2SiO_4 phase to $BaSiO_3$ in the mixed system. In addition, the X-ray diffraction peaks attributed to $Ba_2ZnSi_2O_7$ phase increase with ZnO addition, but the luminescence intensity drops after the maximum value when the amount of ZnO is higher than 150 mol% of BaO. Although, we could not obtain a pure $Ba_2ZnSi_2O_7$ phase for comparison, the photoluminescence of Eu^{2+} in $Ba_2ZnSi_2O_7$ reported in a recent paper indicates that Eu^{2+} in the phase of $Ba_2ZnSi_2O_7$ may also contribute to the photoluminescence in our samples.[25] However, the total intensity of Eu^{2+} luminescence decreases with the increasing $Ba_2ZnSi_2O_7$ phase when the amount of ZnO is above 150 mol% of BaO. Such an effect indicates that the appearance of $Ba_2ZnSi_2O_7$ phase is not the leading mechanism for the drastic enhancement of the Eu^{2+} luminescence. Except with $Ba_2ZnSi_2O_7$, no other phases containing Zn^{2+} have been detected in the samples with ZnO addition, signaling that most of Zn^{2+} ions are not coordinated in other crystalline phases, but present as interstitials in the network of $BaSiO_3$. Furthermore, luminescence enhancement is not observed when a considerable amount of ZnO is added to a pure phase of Ba_2SiO_4:Eu^{2+}. Therefore, it is our hypothesis that the Eu^{2+} luminescence enhancement induced by addition of ZnO in our samples occurs primarily in the phase of $BaSiO_3$:Eu.

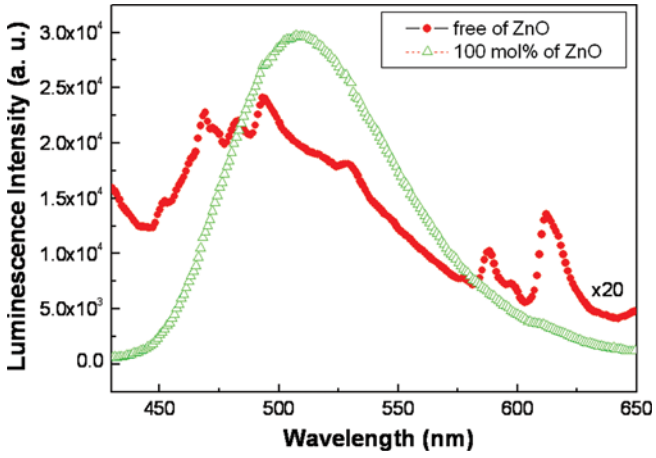

FIGURE 7 Normalized photoluminescence of Eu^{2+} in BaO-SiO_2 system free of ZnO (enlarged by 20 times) and mixed with 100-mol% ZnO of BaO measured at room temperature.

In general, photoluminescence enhancement in luminescent materials resulting from the addition of other components may occur with different mechanisms including primarily (a) charge compensation,[16–18] (b) electron-hole model,[19] (c) dislocation or distortion of crystal structure such as change of structure defects,[20,21] and (d) change of coordination surrounding the activators.[17,22–24] In our experiments, the absence of large shifts or profile changes in emission band indicates that the coordination surrounding Eu^{2+} remained primarily unchanged with addition of ZnO, thus excluding the mechanism c. Because the host ions are divalent, charge compensation is not needed in the system of BZS:Eu^{2+}, if Eu^{2+} replaces Ba^{2+} in the crystalline lattice. However, a large amount of Eu ions may stay as interstitial impurities and have trivalent oxidation states as we can see in the samples without ZnO addition. As shown in Fig. 7, the sharp peaks at 588 and 612 nm are due to the photoluminescence of Eu^{3+} ions in the emission spectrum of the sample without ZnO. The Eu^{3+} peaks disappear in the samples with large amount of ZnO addition. Therefore, charge compensation is a possible mechanism that contributes to the observed luminescence enhancement. In the lattice of $BaSiO_3$, it is also possible that $[SiO_4]^{2-}$ tetrahedrons sharing corners act as electron traps that make Eu^{2+} ions tend to be oxidized into Eu^{3+}. When the sample is excited by a UV light, close multiple anions—that is, $[SiO_4]^{2-}$ tetrahedrons—trap an electron and release a hole to cations such as Ba^{2+} and Eu^{2+}. As a result, quite a fraction of Eu ions presents itself as Eu^{3+} in the lattice without ZnO addition, even though the samples were prepared under reducing atmosphere. This charge-hole mechanism may play a role in preventing Eu^{2+} from ionization. However, such a UV-induced ionization is not observed in the samples without ZnO, and the electron-hole model is not probably the leading mechanism for the observed enhancement. Further investigation is needed to identify the structure of a large quantity of ZnO in the crystal structure of the BSZ system and the mechanisms to support the significant enhancement of Eu^{2+} luminescence.

The decay curves of Eu^{2+} luminescence provide additional insights into the behavior of ZnO addition. As shown in Fig. 8, the luminescence decay time reduces as a function of ZnO addition until the ratio of ZnO:BaO reaches 100%. This effect may be due to two different mechanisms. First, reduction in decay time implies increase in the probability of radiative relaxation, which is consistent with the observed intensity enhancement. This means that, in the presence of ZnO, the local environment of Eu^{2+} is modified in certain degrees so that the cross section of 4f-5d transition increases significantly, but the energy levels (emission wavelength) do not change much. The second possible mechanism is a decrease of Eu^{2+} on trap sites that have longer lifetimes. The nonexponential decay curves also suggest the existence of multiple sites at which Eu^{2+} ions have different luminescence lifetimes. Reducing trap sites would also lead to higher luminescence intensity, because at a trap site, the excitation may end up with a nonradiative relaxation through energy transfer. Furthermore, the photoluminescence of BZS:Eu^{2+} increases with Eu concentration to a maximum when the doped Eu reaches 8 mol% of BaO as shown in Fig. 9. Further increase of Eu concentration leads to decrease of photoluminescence intensity. The concentration quenching is quite a common phenomenon in inorganic luminescent materials that have been doped by rare earth ions and transition metal ions. Excitation energy transferring to the neighboring Eu^{2+} ions leads to nonradiative relaxation or cross-relaxation that quenches the emitting state. It is also observed the luminescence peak at 612 nm increases with Eu concentration, which indicates the increase of Eu^{3+} population.

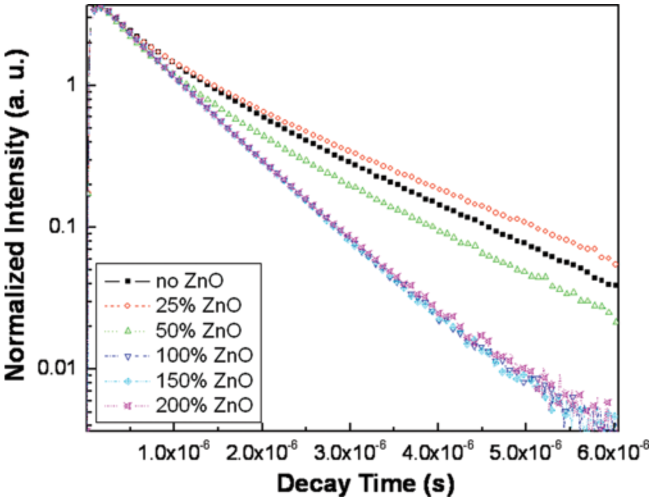

FIGURE 8 Dependence of decay time of Eu^{2+}-doped BaO-SiO_2 system with the content of ZnO mixed.

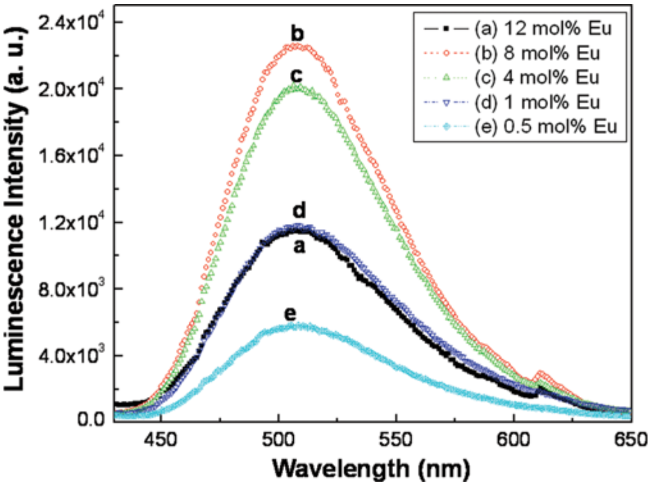

FIGURE 9 Photoluminescence of Eu^{2+}-doped BaO-SiO_2 system mixed with 100-mol% ZnO of BaO varied with Eu^{2+} concentration.

CONCLUSIONS

The present work demonstrates significant improvement of the Eu^{2+} photoluminescence in a BaO-SiO_2 system by mixing ZnO. The optimized luminescent material BZS:Eu^{2+} possesses a potential application in current AlGaN-based UV-LEDs due to its intense absorption band at wavelength region between approximately 380 and 420 nm and its emission band, which is more intense and broader than that of the phosphor Ba_2SiO_4:Eu^{2+}. Eu^{2+} ions in $BaSiO_3$ are inclined to be oxidized due to the chain structure of $BaSiO_3$—in which corner-sharing $[SiO_4]^{2-}$ tetrahedrons trap electrons and release holes to Eu^{2+} ions—and the possibility of interstitial sites. The nonradiative probability resulting from defects is decreased by the addition of ZnO. Further studies are needed to elucidate the form of ZnO in the crystal lattice and the mechanisms responsible for the photoluminescence enhancement of Eu^{2+} with a large addition of ZnO.

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REFERENCES

1. Zhan, K.; Liu, H. Z.; Wu, Y. T.; Hu, W. B. Synthesis of (Y, Gd)$_3$ Al$_5$O$_{12}$:Ce nanophosphor by co-precipitation method and its luminescence behavior. *J. Mater. Sci.* **2007**, *42*, 9200–9204.
2. Pan, Y. X.; Wu, M. M.; Su, Q. Tailored photoluminescence of YAG:Ce phosphor through various methods. *J. Phys. Chem. Solid.* **2004**, *65*, 845–850.
3. Schlotter, P.; Baur, J.; Hielscher, Ch.; Kunzer, M.; Obloh, H.; Schmidt, R.; Schneider, J. Fabrication and characterization of GaN/InGaN/AlGaN double heterostructure LEDs and their application in luminescence conversion LEDs. *Mater. Sci. Engin. B* **1999**, *59*, 390–394.
4. Schlotter, P.; Schmidt, R.; Schneider, J. Luminescence conversion of blue light emitting diodes. *Appl. Phys. A* **1997**, *64*, 417–418.
5. Hao, Z. D.; Zhang, J. H.; Zhang, X.; Sun, X. Y.; Luo, Y. S.; Lu, S. Z. White light emitting diode by using alpha-$Ca_2P_2O_7$:Eu^{2+}, Mn^{2+} phosphor. *Appl. Phys. Lett.* **2007**, *90*, 261113.
6. Le Toquin, R.; Cheetham, A. K. Red-emitting cerium-based phosphor materials for solid-state lighting applications. *Chem. Phys. Lett.* **2006**, *423*, 352–356.
7. Jung, K. Y.; Kim, J. H.; Kang, Y. C. Luminescence enhancement of Eu-doped calcium magnesium silicate blue phosphor for UV-LED application. *J. Lumin.* **2009**, *129*, 615–619.
8. Won, Y. H.; Jang, H. S.; Im, W. B.; Jeon, D. Y.; Lee, J. S. Tunable full-color-emitting $La_{0.827}Al_{11.9}O_{19.09}$:$Eu^{2+}$,$Mn^{2+}$ phosphor for application to warm white-light-emitting diodes. *Appl. Phys. Lett.* **2006**, *89*, 231909.
9. Kim, J. S.; Jeon, P. E.; Choi, J. C.; Park, H. L.; Mho, S. I.; Kim, G. C. Warm-white-light emitting diode utilizing a single-phase full-color $Ba_3MgSi_2O_8$:Eu^{2+}, Mn^{2+} phosphor. *Appl. Phys. Lett.* **2004**, *84*, 2931–2933.
10. Kim, J. S.; Jeon, P. E.; Park, Y. H.; Choi, J. C.; Park, H. L. Color tunability and stability of silicate phosphor for UV-pumped white LEDs. *J. Electrochem. Soc.* **2005**, *152*, H29–H32.
11. Zhang, M.; Wang, J.; Zhang, Q. H.; Ding, W. J.; Su, Q. Optical properties of Ba_2SiO_4:Eu^{2+} phosphor for green light-emitting diode (LED). *Mater. Res. Bull.* **2007**, *42*, 33–39.
12. Kim, J. S.; Park, Y. H.; Kim, S. M.; Choi, J. C.; Park, H. L. Temperature-dependent emission spectra of M_2SiO_4:Eu^{2+} (M = Ca, Sr, Ba) phosphors for green and greenish white LEDs. *Solid State Commun.* **2005**, *133*, 445.
13. Kim, J. S.; Jeon, P. E.; Choi, J. C.; Park, H. L. Emission color variation of M_2SiO_4:Eu^{2+} (M = Ba, Sr, Ca) phosphors for light-emitting diode. *Solid State Commun.* **2005**, *133*, 18.
14. Poort, S. H. M.; Blasse, G. The influence of the host lattice on the luminescence of divalent europium. *J. Lumin.* **1997**, *72–74*, 247–249.
15. Poort, S. H. M.; Reijinhoudt, H. M.; van der Kuip, H. O. T.; Blasse, G. Luminescence of Eu^{2+}- in silicate host lattices with alkaline earth ions in a row. *J. Alloy. Compd.* **1996**, *241*, 75–81.
16. Pan, Y. X.; Liu, G. K. Enhancement of phosphor efficiency via composition modification. *Opt. Lett.* **2008**, *33*, 1816–1818.
17. Okamoto, S.; Yamamoto, H. Characteristic enhancement of emission from $SrTiO_3$:Pr^{3+} by addition of group-IIIb ions. *Appl. Phys. Lett.* **2001**, *78*, 655–657.
18. Liu, J.; Lian, H. Z.; Shi, C. S. Improved optical photoluminescence by charge compensation in the phosphor system $CaMoO_4$:Eu^{3+}. *Opt. Mater.* **2007**, *29*, 1591–1594.
19. Clabau, F.; Rocquefelte, X.; Jobic, S.; Deniard, P.; Whangbo, M.-H.; Garcia, A.; Le Mercier, T. Mechanism of phosphorescence appropriate for the long-lasting phosphors Eu^{2+}-doped $SrAl_2O_4$ with codopants Dy^{3+} and B^{3+}. *Chem. Mater.* **2005**, *15–17*, 3904–3912.
20. Yamamoto, H.; Okamoto, S. Efficiency enhancement by aluminum addition to some oxide phosphors for field emission displays. *Displays* **2000**, *21*, 93–98.
21. Okamoto, S.; Kobayashi, H.; Yamamoto, H. Enhancement of characteristic red emission from $SrTiO_3$:Pr^{3+} by Al addition. *Appl. Phys.* **1999**, *82*, 5594–5596.
22. Debnath, R.; Nayak, A.; Ghosh, A. On the enhancement of luminescence efficiency of Y_2O_3:Eu^{3+} red phosphor by incorporating (Al^{3+}, B^{3+}) in the host lattice. *Chem. Phys. Lett.* **2007**, *444*, 324–327.
23. Shin, S. H.; Kang, J. H.; Jeon, D. Y.; Zang, D. S. Enhancement of cathodoluminescence intensities of Y_2O_3:Eu and Gd_2O_3:Eu phosphors by incorporation of Li ions. *J. Lumin.* **2005**, *114*, 275–280.
24. Gu, Y. X.; Zhang, Q. H.; Li, Y. G.; Wang, H. Z.; Xie, R. J. Enhanced emission from $CaSi_2O_2N_2$:Eu^{2+} phosphors by doping with Y^{3+} ions. *Mater. Lett.* **2009**, *63*, 1448–1450.
25. Yao, S. S.; Xue, L. H.; Li, Y. Y.; You, Y.; Yan, Y. W. Concentration quenching of Eu^{2+} in a novel blue-green emitting phosphor: $Ba_2ZnSi_2O_7$:Eu^{2+}. *Appl. Phys. B* **2009**, *96*, 39–42.