APPLIED PHYSICS LETTERS **91**, 061119 (2007)

# Enhanced luminescence of $SrSi_2O_2N_2:Eu^{2+}$ phosphors by codoping with $Ce^{3+}$, $Mn^{2+}$, and $Dy^{3+}$ ions

Ru-Shi Liu,[a),b)] Yu-Huan Liu, and Nitin C. Bagkar
*Department of Chemistry, National Taiwan University, Taipei 106, Taiwan*

Shu-Fen Hu[a),c)]
*Institute of Electro-Optical Science and Technology, National Taiwan Normal University, Taipei 106, Taiwan*

(Received 6 April 2007; accepted 16 July 2007; published online 9 August 2007)

The authors report here the enhanced luminescence properties of $SrSi_2O_2N_2$ doped with Eu and $M$ ($M$=Ce, Dy, and Mn). The Eu and Eu, Mn-codoped powders were prepared by a solid state reaction at temperatures between 1400 and 1600 °C under $H_2$ (25%)–$N_2$ (75%) atmosphere. The Eu, $M$-codoped $Sr_{1-x-y}Si_2N_2O_2$ phosphors have the monoclinic structure with lattice parameters $a \sim 15.6$ Å, $b \sim 16.2$ Å, $c \sim 9.4$ Å, and $\beta \sim 91°$. The phosphors can be efficiently excited in the UV to visible region, making them attractive as conversion phosphors for a light emitting diode application. A green-yellow emission was observed for Eu,$M$-codoped $Sr_{1-x-y}Si_2N_2O_2$. The addition of $M$ in the Eu site in $SrSi_2O_2N_2$ remarkably enhances the luminescent intensity by the factor of 144%, 148%, and 168% for Ce, Dy, and Mn, respectively. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2768916]

The advantages of light emitting diode (LED)-based white-light sources in comparison with conventional incandescent and fluorescent lamps are longer lifetime, higher efficiency, and better reliability, which promise significant reductions in power consumption and pollution from fossil fuel power plants. Generally, white LED is composed of a yellow phosphor layer, namely, $Ce^{3+}$ doped yttrium aluminum garnet (YAG:Ce) excited by blue LED.[1] White light is generated from the combination of blue and yellow light produced by blue light emitting diode and yttrium aluminum garnet phosphor layer, respectively. The color rendering index ($R_a$) of the YAG-based LED is about 80, which is enough for general illumination. However, it is not suitable for certain medical applications and architectural lighting purposes due to the poor performance of the red component in the spectra. Also, the YAG phosphor has the disadvantage of thermal quenching at high temperature.

Recently, a series of $Eu^{2+}$-activated alkaline earth silicon nitride phosphors, $M_2Si_5N_8$ ($M$=Ca, Sr, and Ba) with red and red-orange emission, has been reported.[2] On the other hand, alkaline earth silicon oxynitride compounds have emerged as superior materials as their composition lies between the oxide compound ($M_2SiO_4$) (Ref. 3) and pure nitride compounds ($M_2Si_5N_8$, $M$=Sr, Ca, and Ba). In this regard, $MSi_2O_2N_2$ phosphor materials with yellow, green to yellow and blue-green emission colors for $M$=Ca, Sr, and Ba, respectively have been studied.[4,5] All these alkaline earth silicon nitride and oxynitride materials have proven to be excellent phosphor materials for white-light LED applications. As expected, the performance of white-light LEDs, such as the color rendition index, color temperature, and color range, can be significantly improved by the combination of the above-mentioned phosphors.

The intensity of emission can be drastically improved in the case of an oxide host matrix by codoping with alkali and rare earth metal ions.[6] The enhanced luminescence on account of codoping in the case of rare earth tantalate[7] and oxide phosphors has been reported.[8] However, there are no reports on the enhanced luminescence in the case of silicon oxynitride phoshors. The objective of the present investigation is to study the effect of doping on the luminescence properties of $SrSi_2N_2O_2:Eu^{2+}$ phosphors. We demonstrate the luminescence properties of $SrSi_2N_2O_2:Eu^{2+}$ phosphors doped with $M$ ($M$=$Ce^{3+}$, $Dy^{3+}$, and $Mn^{2+}$). It was found that the luminescence intensity can be efficiently enhanced by codoping with $Ce^{3+}$, $Dy^{3+}$, and $Mn^{2+}$.

All powder samples $SrSi_2N_2O_2$ doped with Eu and $M$ were synthesized by a high-temperature solid state reaction. The starting materials were high purity $SrCO_3$, $SiO_2$, $Si_3N_4$, $Eu_2O_3$, $Dy_2O_3$, and $MnCO_3$. Stoichiometric homogeneous mixtures of highly pure raw materials were obtained by thorough grinding. The powders were then sintered at 1400–1600 °C for 1 h under reducing atmosphere of $H_2$ (25%)–$N_2$ (75%). The samples were cooled after sintering to room temperature and further characterized by photoluminescence (PL) (FluoroMax-3 & FluoroMax-P) and x-ray diffraction (XRD) (X'Pert PRO advanced automatic diffractometer with Cu$K\alpha$ radiation operated at 45 kV and 40 mA) measurements. The powder XRD of all phosphors indicates single phase formation. Figure 1 shows the powder XRD pattern of $Sr_{0.96}Si_2N_2O_2:Eu_{0.04}$, which is compared with that of $SrSi_2N_2O_2$.[4] All $Sr_{1-x-y}Si_2N_2O_2:Eu_x,M_y$ phosphors crystallize in the monoclinic structure (space group: $P2_1/m$) with lattice parameters $a \sim 15.6$ Å, $b \sim 16.2$ Å, $c \sim 9.4$ Å, and $\beta \sim 91°$.

Figure 2 shows the diffuse reflection spectra of Eu ($x$=0.04) and Ce ($y$=0.04) doped $Sr_{1-x-y}Si_2N_2O_2$. Clearly, these reflection spectra illustrate light absorption in the UV range (<300 nm). The optical absorption edge was found to be 400 and 275–350 nm for Eu and Ce doped $SrSi_2N_2O_2$, respectively. This also indicates that the $Ce^{3+}$ doped sample

---

[a)] Authors to whom correspondence should be addressed.
[b)] Electronic mail: rsliu@ntu.edu.tw
[c)] Electronic mail: sfhu.hu@gmail.com

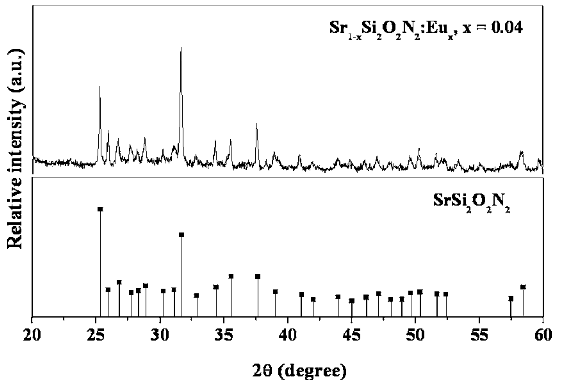

FIG. 1. XRD pattern of $KSr_{1-x}PO_4$:Eu$_x$ as compared to the standard pattern.

can absorb higher energy than the $Eu^{2+}$ doped one.

The excitation spectra of $Sr_{1-x-y}Si_2N_2O_2$:Eu$_x$,Ce$_y$ show a number of broadbands, which can be assigned to the crystal-field components of the 5*d* level in the excited $4f^65d$ transitions of the activator ions. The $Eu^{2+}$-activated $SrSi_2N_2O_2$ phosphor shows a major excitation band at 375 nm and weak shoulder peaks at 320 and 450 nm, whereas $Ce^{3+}$ doped $SrSi_2N_2O_2$ shows a broad peak at 350 nm, in agreement with the obtained diffuse reflection spectra. The enhancement of the absorption intensity by codoping was also found with the optimum $x=0.04$ and $y=0.04$ in $Sr_{1-x-y}Si_2N_2O_2$. All intermediate compositions show broad peaks due to $Ce^{3+}$ and $Eu^{2+}$ in the phosphors. Thus, $Ce^{3+}$ doped $SrSi_2N_2O_2$ can be excited by UV LEDs, whereas the $Eu^{3+}$ or $Eu^{3+}$, $Ce^{3+}$-codoped $SrSi_2N_2O_2$ phosphors can be excited by UV as well as blue LEDs.

Figure 3 demonstrates the emission spectra of $Sr_{1-x-y}Si_2N_2O_2$:Eu$_x$Ce$_y$. For $y=0$, the broadband emission at 540 nm is observed due to the $5d \rightarrow 4f$ transition of the $Eu^{2+}$ activators. However, for $x=0$, the main emission peak of $Ce^{3+}$ in $SrSi_2N_2O_2$ is around 470 nm. For all the intermediate compositions, the position of the emission bands are nearly same with increasing doping concentration of $Ce^{3+}$ in the $Eu^{2+}$ sites. One of the important observations is the increase in the emission intensity as the codopant concentration increases. The maximum emission intensity appeared in $y=0.04$ of $Ce^{3+}$ when the $Eu^{2+}$ concentration was fixed at the *x* value of 0.04. The enhancement is 144% by doping $Ce^{3+}$ in the $Eu^{2+}$ sites of $SrSi_2N_2O_2$ as compared with that of noncodoped one. The reason for the observed enhanced luminescence is the energy transfer from $Ce^{3+}$ to $Eu^{2+}$ in the host lattice of $SrSi_2N_2O_2$. The overlap of $Eu^{2+}$ excitation and $Ce^{3+}$ emission can cause energy transfer from $Ce^{3+}$ to $Eu^{2+}$, which is responsible for the increased luminescence in the case of codoped phosphors. The spectral overlap of normalized PLE and PL of $Sr_{1-x-y}Si_2N_2O_2$:Eu$_x$Ce$_y$ as shown in Fig. 4, is indicative of the energy transfer from a sensitizer to an activator. The inset of Fig. 4 shows the schematic of the energy level system, which describes the energy transfer from $Ce^{3+}$ to $Eu^{2+}$. According to Dexter's theory, the critical distance of energy transfer from $Ce^{3+}$ to $Eu^{2+}$ is defined as the distance for which the probability of transfers equals the probability of radiative emission of $Ce^{3+}$.[9,10] The critical distance of energy transfer from a sensitizer to an activator is given by

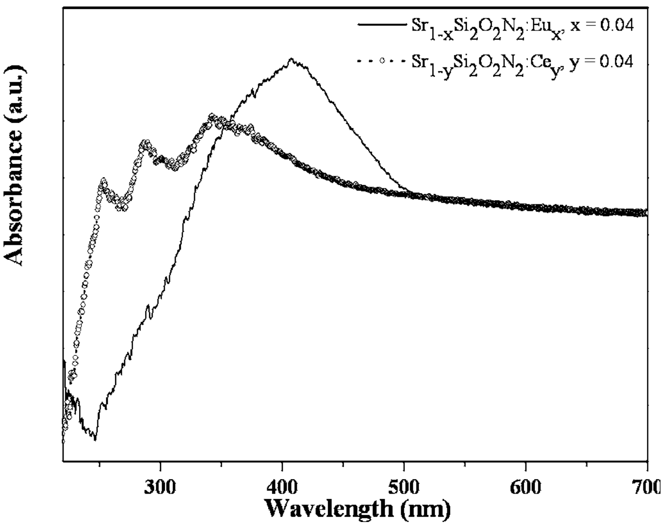

FIG. 2. Diffuse reflection spectra of Eu ($x=0.04$) and Ce ($y=0.04$) doped $Sr_{0.96}Si_2N_2O_2$.

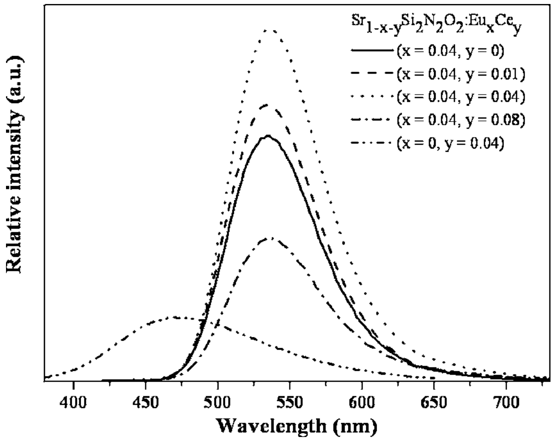

FIG. 3. Emission spectra of $Sr_{1-x-y}Si_2N_2O_2$:Eu$_x$Ce$_y$.

$$R_c^6 = 0.63 \times 10^{28} \frac{4.8 \times 10^{-16} P_A}{E^4} \int f_s(E) F_A(E) dE, \qquad (1)$$

where $P_A$ is the oscillator strength of the transition, which was taken as 0.01 for $Ce^{3+}$ ions, and $R_c$ is the critical distance. The values of *E* (2.567 eV) and spectral overlap ($0.022\ \mathrm{eV}^{-1}$) can be derived from the normalized PLE and

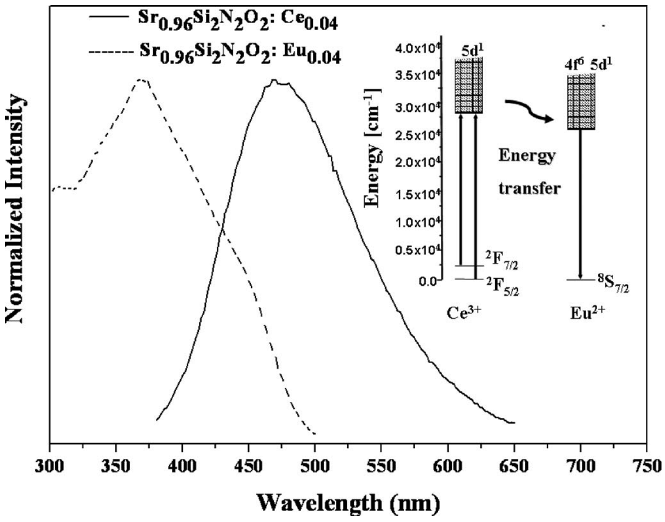

FIG. 4. PLE of $SrSi_2N_2O_2$:Eu and PL spectra of $SrSi_2N_2O_2$:Ce. Inset shows the schematic of the energy level system describing energy transfer in the case of $Sr_{1-x-y}Si_2N_2O_2$:Eu$_x$Ce$_y$.

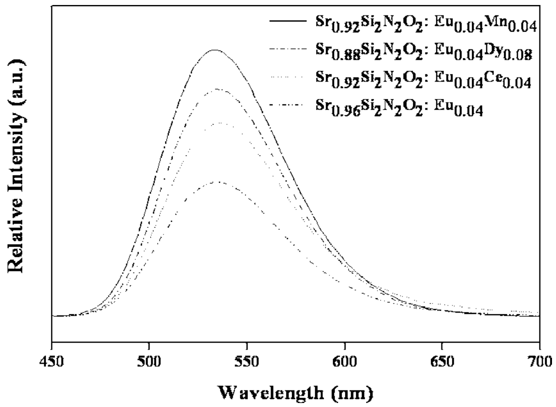

FIG. 5. Emission spectra of $Ce^{3+}$, $Mn^{2+}$, and $Dy^{3+}$ doped and undoped $SrSi_2N_2O_2:Eu^{2+}$.

PL spectra. From Eq. (1) the value of critical constant was calculated as 15.68 Å. The value is similar to the values obtained for $Eu^{2+}$ doping in other host matrices such as silicates and aluminates.[11] We have also investigated the effect of codoping on the luminescence properties of $Eu^{2+}$ doped $SrSi_2N_2O_2$ by $Dy^{3+}$ and $Mn^{2+}$ ions. The excitation and emission spectra of $Dy^{3+}$ and $Mn^{2+}$ doped $SrSi_2N_2O_2Eu^{2+}$ phosphors are essentially the same as those observed for $Ce^{3+}$ doped $SrSi_2N_2O_2:Eu^{2+}$. Figure 5 shows the comparison of emission intensity for $Ce^{3+}$, $Dy^{3+}$, and $Mn^{2+}$ doped and undoped $SrSi_2N_2O_2:Eu^{2+}$ phosphors. The emission intensity is increased by 144%, 148%, and 168% as compared to intensity of $Eu^{2+}$ doped $SrSi_2N_2O_2$ for $Ce^{3+}$, $Dy^{3+}$, and $Mn^{2+}$ samples, respectively. The maximum intensity is observed for $Mn^{2+}$ doped $SrSi_2N_2O_2:Eu^{2+}$ phosphors.

In conclusion, the present work demonstrates the effect of codoping on the luminescence properties of $SrSi_2O_2N_2:Eu^{2+}$ phosphors. The photoluminescence intensity of the $SrSi_2O_2N_2:Eu^{2+}$ phosphor is increased as the concentration of codopant increases in the host matrix. The highest photoluminescence intensity was observed for $Mn^{2+}$ doped $SrSi_2O_2N_2:Eu^{2+}$ phosphors. $SrSi_2O_2N_2:Eu^{2+}$ doped with rare earth ions with considerable enhanced emission intensity can be useful for white LEDs.

The authors would like to acknowledge the financial support from the National Science Council of Taiwan (Contract Nos. 95-2113-M-002-009 and 95-2112-M-003-125) and the Economic Affair of Taiwan (Contract No. 95-EC-17-A-07-S1-043).

[1] M. Yamada, Y. Narukawa, and T. Mukai, Jpn. J. Appl. Phys., Part 2 **41**, L246 (2002).
[2] H. A. Hoppe, H. Lutz, P. Morys, W. Schnick, and A. Seilmeier, J. Phys. Chem. Solids **61**, 2001 (2000).
[3] J. S. Kim, P. E. Jeon, J. C. Choi, and H. L. Park, Solid State Commun. **133**, 187 (2005).
[4] Y. Q. Li, A. C. A. Delsing, G. De With, and H. T. Hintzen, Chem. Mater. **17**, 3242 (2005).
[5] Y. Q. Li, G. De With, and H. T. Hintzen, J. Mater. Chem. **15**, 4492 (2005).
[6] J. C. Park, H. K. Moon, D. K. Kim, S. H. Byeon, B. C. Kim, and K. S. Suh, Appl. Phys. Lett. **77**, 2162 (2000).
[7] M. Gu, L. Xiao, X. Liu, R. Zhang, B. Liu, and X. Xu, J. Alloys Compd. **426**, 390 (2006).
[8] L. Wanga and Y. Wang, J. Lumin. **122**, 921 (2007).
[9] D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).
[10] X. Liu, C. Lin, and J. Lin, Appl. Phys. Lett. **90**, 081904 (2007).
[11] G. Blasse, Philips Res. Rep. **24**, 131 (1969).