



Synthesis and Characterization of Novel Nitride Phosphors $\text{Ca}_5\text{Si}_2\text{N}_6: \text{Eu}^{2+}/\text{Ce}^{3+}$

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The novel nitride phosphor $\text{Ca}_5\text{Si}_2\text{N}_6: \text{Eu}^{2+}/\text{Ce}^{3+}$ were successfully synthesized at 1450 °C *via* a solid-state reaction method under a nitrogen atmosphere. The photoluminescence of $\text{Ca}_5\text{Si}_2\text{N}_6: \text{Eu}^{2+}/\text{Ce}^{3+}$ shows that the phosphors have the main emission peak at 609 and 470 nm, respectively. The phosphor $\text{Ca}_5\text{Si}_2\text{N}_6: \text{Eu}^{2+}$ can be excited in the range from 350 to 480 nm, which makes it the attractive candidate phosphors for the application in phosphor-converted light-emitting diodes as red phosphors. The $\text{Ca}_5\text{Si}_2\text{N}_6: \text{Ce}^{3+}$ can be effectively excited by near ultraviolet. Moreover, the effect of doping concentration on the luminescence property is investigated.

Keywords: Silicon oxynitride, Phosphors, Photoluminescence, Energy transfer.

INTRODUCTION

In recent years, white light-emitting diodes (W-LEDs) have attracted much attention because of their long lifetime, high efficiency, less toxicity and positive environmental effects as a light source for the next-generation of the solid-state light and other potential applications, such as backlight source for liquid crystal displays and so on. A variety of materials and device configurations have been attempted to realize the fine properties of white-light-emitting diodes^{1,2}.

The white light can be achieved by the following methods. The first way is to combine a blue GaN light-emitting diode chip with a yellow phosphor, such as YAG:Ce³⁺ phosphor. The second way is to combine the three primary colour phosphors with a near ultraviolet (UV) light-emitting diode. In the first way, the drawbacks include a low-rendering index and a high colour temperature due to the deficiency of red emission in the visible spectrum. In order to achieve high colour rendering index and sufficient colour reproducibility, it is desired to develop highly-efficient red phosphors with sufficient chemical durability and ideal luminescent properties. As for the second method, the development of high quality three primary colour phosphors is necessary^{3,4}. Recently, silicon-oxynitride and silicon-nitride have received remarkable attention as host materials for rare earth doped phosphors for using wavelength conversion phosphors for near-UV or blue-light-emitting diode owing to their outstanding thermal and chemical stability⁵⁻⁸.

Generally speaking, under UV or blue light excitation, Eu²⁺ doped silicon-oxynitride or silicon-nitride can emit blue to yellow light^{9,10} and Ce³⁺ doped silicon-oxynitride or silicon-

nitride show blue emission¹¹. In this paper, the novel red emission of Eu²⁺ doped silicon-nitride and blue emission of Ce³⁺ doped silicon-nitride are obtained.

In this work, Eu²⁺/Ce³⁺ doped $\text{Ca}_5\text{Si}_2\text{N}_6$ was prepared by using stable raw materials at relatively low temperature *via* solid-state reaction and the luminescence properties were investigated. They are also suitable to be wavelength conversion phosphors.

EXPERIMENTAL

The phosphors were prepared in a horizontal tube furnace [CVD(G)-06/30/1, Hefei Risine Heatek Co. Ltd., China] and the raw materials Ca₃N₂ (99.9 %), α-Si₃N₄ (99.9 %), Eu₂O₃ (99.99 %) and CeO₂ (99.99 %) were weighed in stoichiometric proportions. The raw materials were mixed in an agate mortar and filled into a corundum crucible. After the putting of the mixed raw materials. After that the chamber was pumped to a pressure of less than 6 × 10⁻³ Pa by a diffusion pump and then refilled with pure N₂. Subsequently, the mixed powder was pre-heated at 900 °C (the temperature was increased at a rate of 10 °C/min) for 1 h to ensure the decomposition of CaCO₃, then the temperature was increased to 1450 °C (at a rate of 3 °C/min) and maintained for 4 h. After reaction, the samples were cooled down to 900 °C (at a rate of 3 °C/min) and cooled to room temperature finally.

The structures of the samples were investigated *via* an X-ray diffractometer (XRD, D8 ADVANCE) using CuK_α radiation (λ = 0.15406 nm). The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were charac-

terized using a FLS920. All the measurements were done on powders and at room temperature.

RESULTS AND DISCUSSION

The XRD patterns of $\text{Ca}_5\text{Si}_2\text{N}_6: \text{Eu}^{2+}/\text{Ce}^{3+}$ (Fig. 1) showed that $\text{Ca}_5\text{Si}_2\text{N}_6$ was the majority phase besides a Ca_3N_2 phase and a Si_3N_4 phase. The two impurity phases maybe come from the incompleting reaction. The $\text{Ca}_5\text{Si}_2\text{N}_6$ can be classified as monoclinic family and was indexed with the unit cell parameter $a = 16.3755 \text{ \AA}$, $b = 11.2864 \text{ \AA}$ and $c = 10.1666 \text{ \AA}$ with the space group C2/c^{15} .

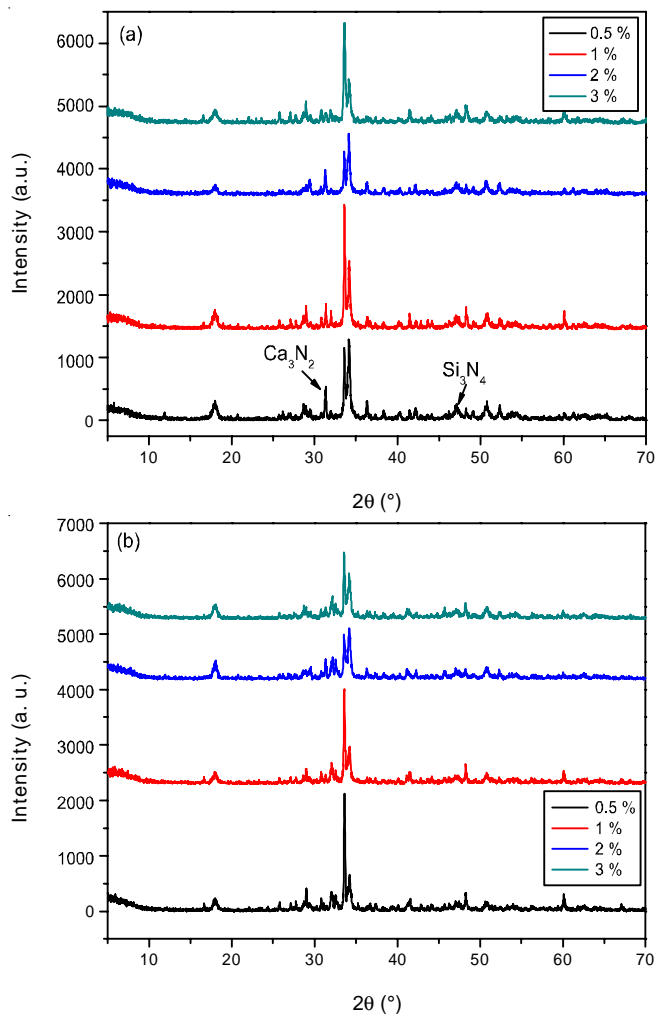


Fig. 1. XRD patterns of $\text{Ca}_5\text{Si}_2\text{N}_6: \text{Eu}^{2+}$ (a) and $\text{Ca}_5\text{Si}_2\text{N}_6: \text{Ce}^{3+}$ (b) with different doping concentrations

The photoluminescence and photoluminescence excitation spectra of the $\text{Ca}_5\text{Si}_2\text{N}_6: \text{Eu}^{2+}/\text{Ce}^{3+}$ (1 at. %) are shown in Fig. 2. For the $\text{Ca}_5\text{Si}_2\text{N}_6: \text{Eu}^{2+}$, the photoluminescence spectrum exhibits a single intense red emission centered at 609 nm and the full width of half emission maximum is of about 120 nm. The broad excitation spectrum expands from 350 to 480 nm and the two spectra overlap very small. To obtain an applicable phosphor, it can be combined with a blue chip for red emission. As to the $\text{Ca}_5\text{Si}_2\text{N}_6: \text{Ce}^{3+}$, the 470 and 442 nm emission are obtained and the excitation peak locates at 350 nm. It can be used in near UV excitation light-emitting diode for blue emission.

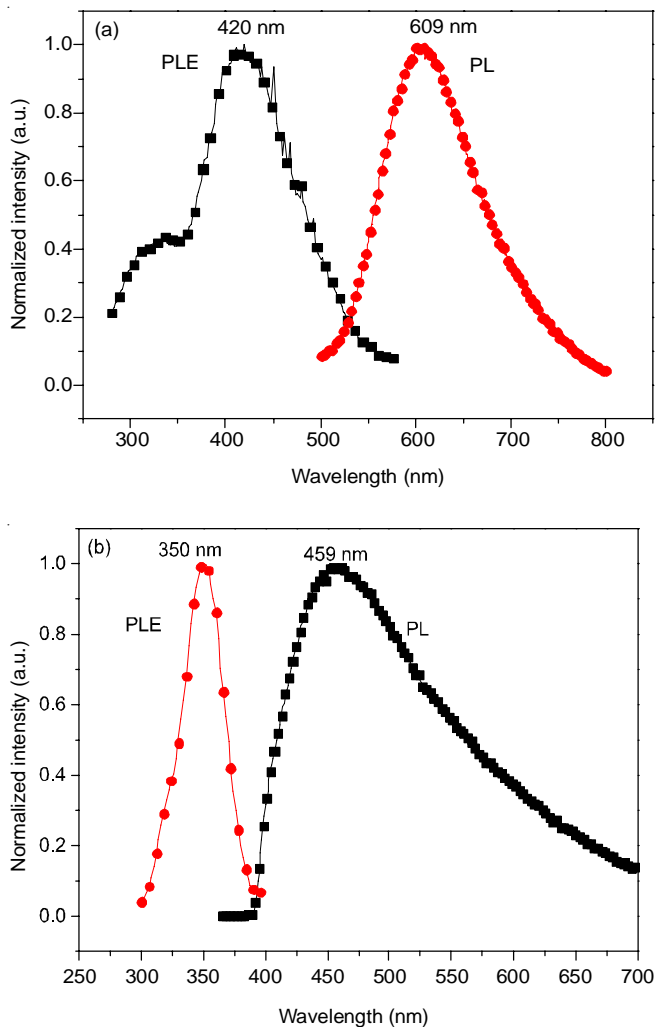


Fig. 2. Excitation and emission spectra of $\text{Ca}_5\text{Si}_2\text{N}_6: \text{Eu}^{2+}$ (a) and $\text{Ca}_5\text{Si}_2\text{N}_6: \text{Ce}^{3+}$ (b) with the concentration 1 at. %

The emission spectra of $\text{Ca}_5\text{Si}_2\text{N}_6: \text{Eu}^{2+}/\text{Ce}^{3+}$ phosphors with the Eu^{2+} or Ce^{3+} concentrations of 0.5 at. %, 1 at. %, 2 at. % and 3 at. % is shown in Fig. 3. The emission intensity decreases with the increased $\text{Eu}^{2+}/\text{Ce}^{3+}$ concentration. The decreased intensity results from concentration quenching which is from non-radiative energy transfer among luminescent centers. The increased $\text{Eu}^{2+}/\text{Ce}^{3+}$ concentrations make the distances shortening and probability of energy transfer increasing. So the probability of energy transfer between luminescent center and quenching center is increased. Finally, the emission intensity is decreased. In the non-radiative energy transfer, the multipolar-multipolar interaction which is dependent on the distance among $\text{Eu}^{2+}/\text{Ce}^{3+}$ ions, should be predominantly considered for the energy transfer among $\text{Eu}^{2+}/\text{Ce}^{3+}$ ions.

The positions of the peaks shift from 603 to 616 nm and from 451 to 456 nm for Eu^{2+} , Ce^{3+} doped $\text{Ca}_5\text{Si}_2\text{N}_6$, respectively. The $5d$ levels of Eu^{2+} split easily because there is no shield effect from the outer environment. Moreover, the electron cloud expansion effect can make the splitting of $5d$ levels and lower the energy of barycenter of $5d$ states. So the red-shift occurs. The same case happens on the Ce^{3+} .¹²⁻¹⁵ Moreover, energy transfer can also cause a red-shift^{16,17}.

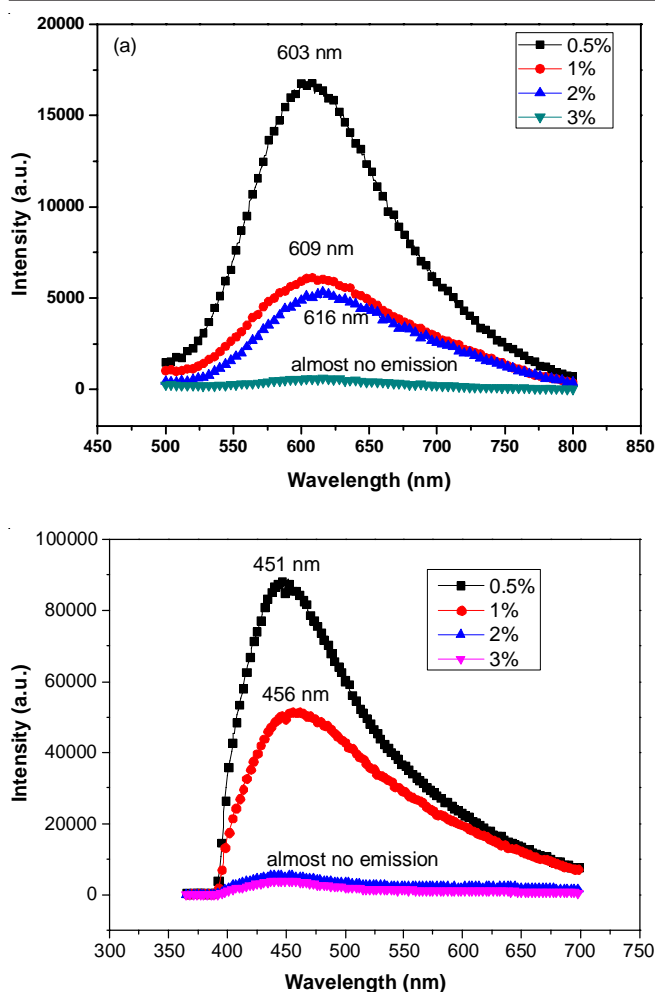


Fig. 3. Emission spectra of $\text{Ca}_5\text{Si}_2\text{N}_6:\text{Eu}^{2+}$ (a) and $\text{Ca}_5\text{Si}_2\text{N}_6:\text{Ce}^{3+}$ (b) with different concentration

Conclusion

$\text{Ca}_5\text{Si}_2\text{N}_6:\text{Eu}^{2+}/\text{Ce}^{3+}$ phosphors which present the red and blue emission were synthesized *via* a solid-state reaction method. The results indicate the produced phosphors to be promising materials for blue/near UV chips based light-emitting diodes. The energy transfer which is governed by

multipolar-multipolar interactions results in red-shift and concentration quenching with increased $\text{Eu}^{2+}/\text{Ce}^{3+}$ concentration.

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REFERENCES

1. C.Y. Liu, Z.G. Xia, Z.P. Lian, J. Zhou and Q.F. Yan, *J. Mater. Chem. C*, **1**, 7139 (2013).
2. X. Zhang, Z. Zhao, X. Zhang, A. Marathe, D.B. Cordes, B. Weeks and J. Chaudhuri, *J. Mater. Chem. C*, **1**, 7202 (2013).
3. R.J. Xie and N. Hirosaki, *Sci. Technol. Adv. Mater.*, **8**, 588 (2007).
4. S.F.X. Ye, F. Xiao, Y.X. Pan, Y.Y. Ma and Q.Y. Zhang, *Mater. Sci. Eng. Rep.*, **71**, 1 (2010).
5. P.F. Smet, K. Van den Eeckhout, A.J.J. Bos, E. van der Kolk and P. Dorenbos, *J. Lumin.*, **132**, 682 (2012).
6. J.Y. Tang, C. Zhan, L.X. Yang, L.Y. Hao, X. Xu and A. Simeon, *Mater. Chem. Phys.*, **132**, 1089 (2012).
7. T. Suehiro, N. Hirosaki and R.-J. Xie, *ACS Appl. Mater. Interfaces*, **3**, 811 (2011).
8. M. Seibald, T. Rosenthal, O. Oeckler, C. Maak, A. Tücks, P.J. Schmidt, D. Wiechert and W. Schnick, *Chem. Mater.*, **25**, 1852 (2013).
9. X.F. Song, H. He, R.L. Fu, D.L. Wang, X.R. Zhao and Z.W. Pan, *J. Phys. D Appl. Phys.*, **42**, 065409 (2009).
10. Y.A. Zhang, X.T. Liu, B.F. Lei, H.E. Wang and Q.M. Sun, *Energy Procedia*, **16**, 391 (2012).
11. Y. Fang, Y.Q. Li, R.J. Xie, N. Hirosaki, T. Takade, X.Y. Li and T. Qiu, *J. Solid State Chem.*, **184**, 1405 (2011).
12. K.Y. Jung and J.H. Seo, *Electrochem. Solid. State*, **11**, J64 (2008).
13. J.K. Park, J.M. Kim, E.S. Oh and C.H. Kim, *Electrochem. Solid. State*, **8**, H6 (2005).
14. H.A. Hoppe, H. Lutz, P. Morys, W. Schnick and A. Seilmeier, *J. Phys. Chem. Solids*, **61**, 2001 (2000).
15. Y. Kaneko and T. Koda, *J. Cryst. Growth*, **86**, 72 (1990).
16. Y.Q. Li, N. Hirosaki, R.J. Xie, T. Takeda and M. Mitomo, *Chem. Mater.*, **20**, 6704 (2008).
17. C.J. Duan, X.J. Wang, W.M. Otten, A.C.A. Delsing, J.T. Zhao and H.T. Hintzen, *Chem. Mater.*, **20**, 1597 (2008).