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Letter

Simultaneous tuning for excitation and emission of N doped Sr_2SiO_4:Eu for white light LEDs

Yunxin Gu[a], Qinghong Zhang[a], Yaogang Li[b,*], Hongzhi Wang[a,*]

[a] *State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, China*
[b] *Engineering Research Center of Advanced Glasses Manufacturing Technology, Ministry of Education, China*

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ABSTRACT

Tunable color point and efficient excitation are two important challenges for improving white light LEDs. In this paper, red-shift in the emission spectra of Sr_2SiO_4:Eu has been achieved, and the excitation band has been tuned to fit the blue LED chips simultaneously by doping N into the host. XRD results showed that the unit cell volume markedly increased after nitridation. Moreover, nitridation resulted in the increase in weight loss, which can be attributed to the substitute of Si–O bonds by Si–N bonds. The effect of nitridation on the luminescence properties was well discussed.

1. Introduction

With the development of solid state lighting, a mount of phosphor systems have been developed to generate white light by coupling UV- and blue LED chips. Among them, Eu^{2+} or Ce^{3+} doped oxides are most widely applied, and the outstanding example is YAG:Ce^{3+}. However, the 5d electrons of Eu^{2+} and Ce^{3+} ions were unshielded from the crystal field by the 5s and 5p electrons when in the excited state, and the excitation and emission spectra can hardly reach the long wavelength in the oxide hosts, which have low covalence and small crystal-field splitting [1–3]. Sulfide phosphors are traditional series with long emission wavelength (i.e., SrS:Eu^{2+} and CaS:Eu^{2+}), but these materials suffer from low chemical stability in LEDs environment [4–6]. Nitride phosphors are more stable and more efficient, but the synthesis of these materials requires high reaction temperatures, high pressure and high-purity nitride starting materials, which become obstacles for the further application [7–9]. Thus, it is necessary and challengeable to shift the emission wavelength of the oxide phosphors to the long wavelength.

Rare-earth doped silicates are well-developed phosphors, which are widely applied in fluorescent lamps. The Eu^{2+} emission varies from ultraviolet to yellow, depending on the size of the cation. Among them, Sr_2SiO_4:Eu^{2+} has a relatively long emission wavelength, and shows promising prospect in producing white light using the GaN blue LED [10–16]. It can be a good candidate for the yellow-red phosphor after shifting the emission band to the longer wavelength.

However, the maximum excitation band of Sr_2SiO_4:Eu is around 370 nm, too short for the blue LED chip. Park et al. improved the absorption in the rang of 450–470 nm by co-doping Mg and Ba ions, but this doping resulted in the blue-shift of the emission wavelength [17].

In this work, we attempt to tune the excitation and emission of Sr_2SiO_4:Eu simultaneously by doping N ions. Emphasis is placed on the effects of nitridation on the PL properties and crystal structures of N doped Sr_2SiO_4:Eu phosphors.

2. Experimental

N doped Sr_2SiO_4:Eu was prepared by a solid-state reaction. Appropriate amounts of the starting materials of $SrCO_3$, SiO_2 and Eu_2O_3 were weighted and mixed in ethanol solution using an agate mortar. After drying, the mixture was loaded into an Al_2O_3 boat and fired in a horizontal tube furnace at different temperatures for 2 h under NH_3 flow (caution: NH_3 gas is pungent and improper use at high temperature will lead blast!). After the predetermined reaction time, the sample was furnace cooled in NH_3 atmosphere.

X-ray diffraction (XRD) was carried out on a Rigaku-D/max 2550 PC diffractometer with Cu-K_α radiation ($\lambda = 0.15405$ nm). Lattice parameters determination was carried out by the least-squares method from X-ray diffraction data collected in the range 10–80° in 2θ by a step-scan mode with a step size of 0.02 and a count time of 1 s per step. The fraction of weight loss in the nitridation reaction and in the reduction reaction ($\Delta W_{\text{nitridation}}/\Delta W_{\text{reduction}}$) was calculated for each run, which corresponds to the extent of nitridation. The loss on ignition of the starting powder was predetermined and was taken into account. The photoluminescence (PL) spectra and the efficiency were measured at room temperature using a fluorescent spectrophotometer JASCO FP-6600 with an integrating sphere.

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* Corresponding authors. Tel.: +86 21 67792881; fax: +86 21 67792855.
E-mail addresses: yaogang_li@dhu.edu.cn (Y. Li), wanghz@dhu.edu.cn (H. Wang).

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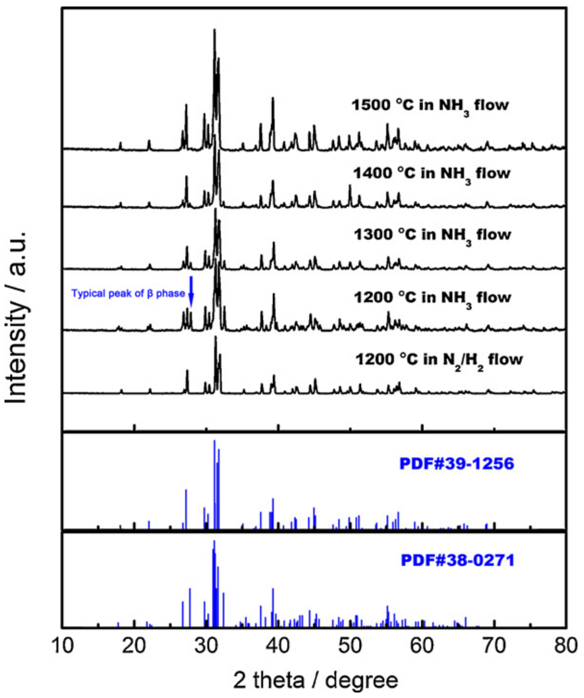

Fig. 1. XRD patterns of the samples treated at different temperatures and different atmospheres.

3. Results and discussion

Strontium orthosilicate has a high-temperature orthorhombic (α-Sr_2SiO_4, PDF#39-1256) and a low-temperature monoclinic phase (β-Sr_2SiO_4, PDF#38-0271). In this work, the samples prepared at 1200 °C in N_2 (95%)–H_2 (5%) were in α-Sr_2SiO_4 phase and no impurity phase was observed in Fig. 1. In contrast, the transition from β- to α-Sr_2SiO_4 in NH_3 flow was not completed until 1500 °C. A mount of β-phase in the samples treated at 1200 °C was observed and a trace of β-phase was still remained at 1400 °C. This can be attributed to the nitridation in NH_3 atmosphere which consumed extra energy, resulting in the increase in the phase transition temperature.

Table 1 shows the lattice parameters and the weight loss of different samples. The unit cell volume markedly increased after nitridation, and continuously increased when a higher temperature was employed. This may indicate that Si–O was replaced by Si–N in the lattice of Sr_2SiO_4, because the bond length of Si–N (1.74 Å) [7] is much longer than that of Si–O (1.61 Å) [18]. The increase in weight loss after nitridation reaction provided additional evident from another point of view, because N is lighter than O. When O was partially replaced by N, the weight loss of reaction increased.

Fig. 2 shows the PL spectra of samples treated in reduction atmosphere and different nitridation conditions. No significant red-shift was observed in the emission peaks excited at 370 nm. All samples show the typical emission bands at around 540 nm, originating from the 4f to 5d transition of Eu^{2+} ions. But it should be noticed that the samples treated in NH_3 atmosphere show weak shoulders between 400 nm and 480 nm. This may be attributed to the appearance of the β-phase.

When the samples were excited at 450 nm, it can be found that the emission peak of samples prepared in reduction atmosphere shifted from 537 nm to 540 nm and the samples treated in the NH_3 atmosphere shifted to longer wavelength. Meanwhile, wide shoulders between 550 and 650 nm appeared in the samples treated in the NH_3 atmosphere. These emission spectra can be better appreciated after Gaussian fitting.

In Fig. 3, three typical samples which had obvious changes were selected. All the three emission bands can be separated into two Gaussians. One was at short wavelength (maxima at about 535–545 nm) and the other was at long wavelength (maxima at about 570–590 nm). After nitridation in NH_3 atmosphere, both of the two Gaussians shifted to the red direction. The nitridation temperature was higher, the shifted wavelength was larger.

The red-shift in the emission can be mainly attributed to substitution of the Si–O bonds by the Si–N bonds. Because the N^{3-} has higher formal charge and the nephelauxetic effect is more serious compared with O^{2-}, the crystal-field splitting of the 5d levels of Eu^{2+} is larger and the center of gravity of the 5d states shift

Table 1
Lattice parameters and weight loss of samples treated at different conditions. $\Delta W_{nitridation}$ and $\Delta W_{reduction}$ mean the weight loss in the nitridation reaction and in the reduction reaction, respectively.

Samples	Cell parameter (Å)			Cell volume (Å^3)	$\Delta W_{nitridation}/\Delta W_{reduction}$
	a	*b*	*c*		
1200 °C in N_2/H_2 flow	7.06131	5.65302	9.7112	387.65	1.00
1200 °C in NH_3 flow	7.06477	5.65367	9.72503	388.44	1.01
1300 °C in NH_3 flow	7.07759	5.65563	9.72201	389.16	1.03
1400 °C in NH_3 flow	7.07766	5.66332	9.74082	390.44	1.04
1500 °C in NH_3 flow	7.07912	5.67236	9.74301	391.23	1.05

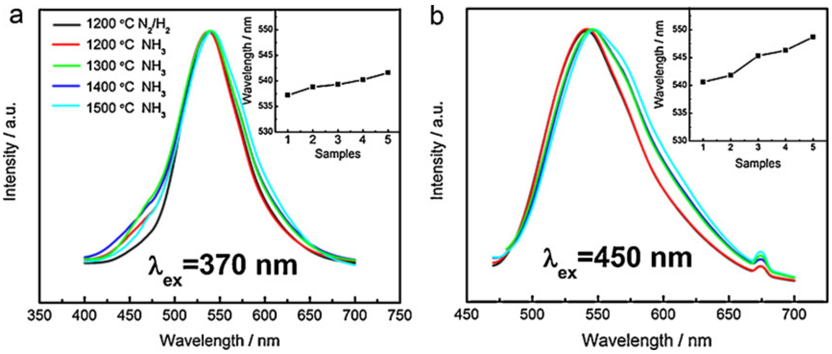

Fig. 2. Emission spectra excited at 370 nm (a) and 450 nm (b) of the samples treated at different temperatures and different atmosphere.

Table 2
Luminescence properties of samples treated at 1200 °C in different atmospheres with different holding times. (The absorption coefficient means the ratio of the photon number of excitation light absorbed by the sample to the photon number of excitation light irradiated to the sample.).

Samples	Emission wavelength (nm)	Emission intensity (a.u.)	Absorption coefficient (%)	External quantum efficiency (%)
1200 °C, 2 h in N_2/H_2 flow	540.6	716.3	32.6	27.4
1200 °C, 2 h in NH_3 flow	541.8	728.2	58.6	28.1
1200 °C 10 h in NH_3 flow	545.7	813.1	65.8	33.4

Luminescence properties above were all measured under 450 nm.

to lower energies (i.e., longer wavelength) than in an analogous oxygen environment.

Moreover, it should be noticed that between the two Gaussians, the red-shift in long wavelength is more significant than that in short wavelength, which implies the preference of the substitution for Si–O bonds by Si–N bonds in different crystal sites.

In Sr_2SiO_4, there are two cation sites of Sr^{2+}, which are ten-coordinated (Sr I) and nine-coordinated (Sr II) by oxygen atoms, respectively. When the Sr_2SiO_4 host was doped with Eu^{2+} ions, Eu^{2+} would occupy both of the two Sr^{2+} randomly and exhibit two different emission bands at around 460–490 nm (excited at 320 nm) and 540–570 nm (excited at 370 nm). In this work, the emission band obtained at 450 nm may be originated from both of Eu(I) and Eu(II). After nitridation, there were more O ions substituted by N ions around Eu(II) sites than that around Eu(I) sites. Hence, the emission bands originated from Eu(II) sites showed more obvious red-shift than that originated from Eu(II) sites.

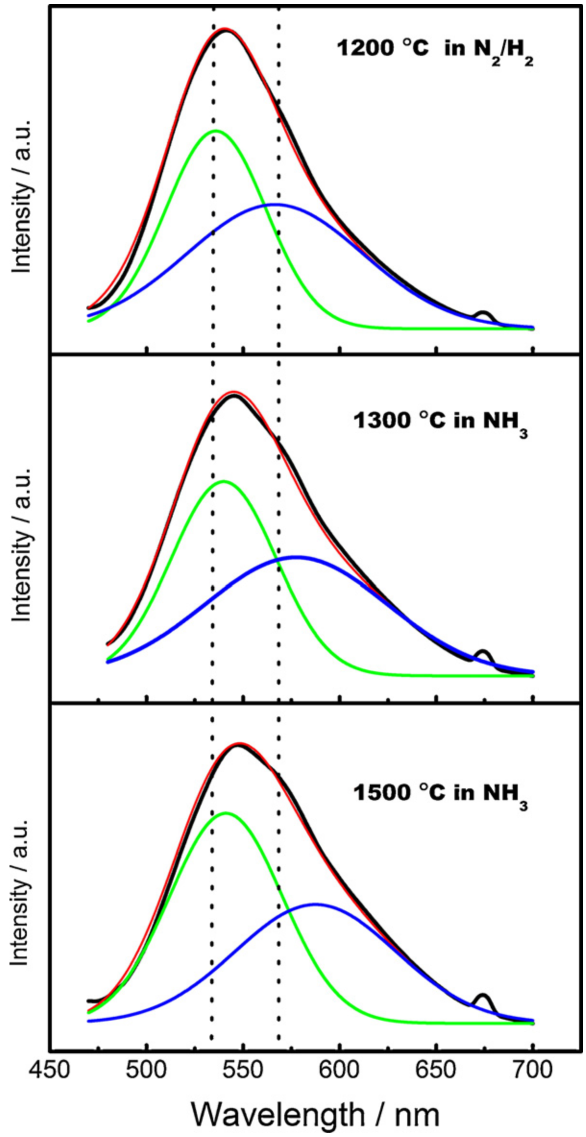

Fig. 3. Gaussian fits of the emission spectra of the samples excited at 450 nm. Black lines are the experimental results, and red lines are the fitting results composed of blue lines and green lines, which are two Gaussian peaks. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

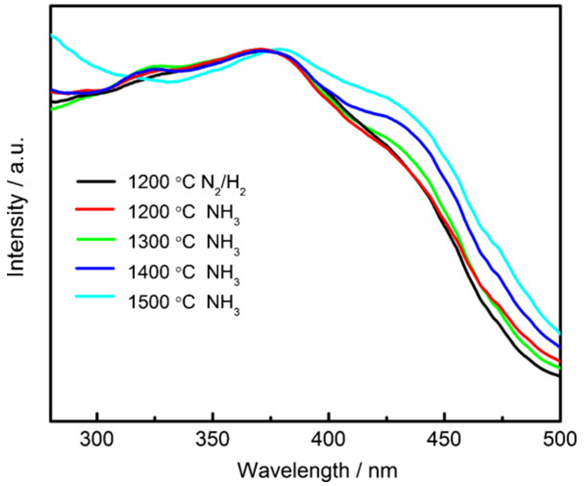

Fig. 4. Excitation spectra of samples treated at different conditions (λ_{em} = 560 nm).

Red-shift also occurs in the excitation spectra in Fig. 4. Comparing with the sample treated in the reduction atmosphere, the excitation peak of the sample treated at 1400 °C in NH_3 shifted from 370 nm to 380 nm. Moreover, after nitridation, a shoulder appeared at 400–450 nm, and the intensity of the shoulder increased with the nitridation temperature. The red-shift of the peak around 375 nm suggested that the conduction band of N doped Sr_2SiO_4 was laid in a lower state when Si–O bonds were partially substituted by the Si–N bonds, and the increase in the intensity between 400 and 450 nm can be attributed to the enhancement of direct excitation from the Eu^{2+} ions.

Besides the heating temperature, the nitridation process was also influenced by the holding time. Table 2 shows the luminescence properties of samples prepared in different conditions. It can be observed that the emission peak of the sample shifted to longer wavelength when a longer holding time was employed. Emission intensity and external quantum efficiency can be also improved, especially after long time nitridation, which may be attributed to the better crystallization. It is noteworthy that the absorption at 450 nm of the sample after nitridation greatly increased. This may be because the doped N ion can shorten the energy band gap of the host.

4. Conclusions

N doped Sr_2SiO_4:Eu phosphors were synthesized by solid state reaction in NH_3 atmosphere. The increases in weight loss and the lattice expansions indicated that N ion had been doped into the lattice. After nitridation, the emission spectra had been tuned to the longer wavelength and the excitation band around 450 nm had been enhanced to fit the blue LED chips. It shows to be a promising method to have long wavelength emission from the oxides and tune the excitation bands at the same time.

Acknowledgments

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References

[1] D.H. Gahane, N.S. Kokode, P.L. Muthal, S.M. Dhopte, S.V. Moharil, J. Alloys Compd. 484 (2009) 660.
[2] C.F. Guo, Y. Xu, F. Lv, X. Ding, J. Alloys Compd. 497 (2010) L21.
[3] Z.C. Wu, J. Liu, W.G. Hou, J. Xu, M.L. Gong, J. Alloys Compd. 498 (2010) 139.
[4] N. Avci, J. Musschoot, P.F. Smet, K. Korthout, A. Avci, C. Detavernier, D. Poelman, J. Electrochem. Soc. 156 (2009) J333.
[5] S.H. Yoo, C.K. Kim, J. Electrochem. Soc. 156 (2009) J170.
[6] Y. Kojima, T. Toyama, J. Alloys Compd. 475 (2009) 524.
[7] K. Shioi, Y. Michiue, N. Hirosaki, R.J. Xie, T. Takeda, Y. Matsushita, M. Tanaka, Y.Q. Li, J. Alloys Compd. 509 (2011) 332.
[8] K. Shioi, N. Hirosaki, R.J. Xie, T. Takeda, Y.Q. Li, J. Alloys Compd. 504 (2010) 579.
[9] X.W. Zhu, Y. Masubuchi, T. Motohashi, S. Kikkawa, J. Alloys Compd. 489 (2010) 157.
[10] A. Nag, T.R.N. Kutty, J. Mater. Chem. 14 (2004) 1598.
[11] J.S. Kim, P.E. Jeon, J.C. Choi, H.L. Park, Solid State Commun. 133 (2005) 187.
[12] X.Y. Sun, J.H. Zhang, X. Zhang, Y.S. Luo, X.J. Wang, J. Rare Earths 26 (2008) 421.
[13] H. He, R.L. Fu, X.F. Song, D.L. Wang, J.K. Chen, J. Lumin. 128 (2008) 489.
[14] C.-H. Lu, P.-C. Wu, J. Alloys Compd. 466 (2008) 457.
[15] J.H. Lee, Y.J. Kim, Mater. Sci. Eng. B 146 (2008) 99.
[16] W.-H. Hsua, M.-H. Sheng, M.-S. Tsai, J. Alloys Compd. 467 (2009) 491.
[17] J.K. Park, K.J. Choi, S.H. Park, C.H. Kim, H.K. Kim, J. Electrochem. Soc. 152 (2005) H121.
[18] É.I. Yurieva, A.L. Ivanovskii, J. Struct. Chem. 41 (2000) 56.