Advanced Materials Research *Online: 2013-05-14*
ISSN: 1662-8985, Vols. 690-693, pp 555-558
doi:10.4028/www.scientific.net/AMR.690-693.555

Emission color variation of $Sr_3SiO_5:Ce^{3+}$, Li^+ phosphor for near-UV light-emitting diodes by co-doping with Mg^{2+} and Ba^{2+}

Pingping Zhu[1, a], Tongwen Huang[2,b], Xiaojun Wang[3,c], Huili Li[4,d,*], and Zhuo Sun[5,e]

[1-5] Engineering Research Center for Nanophotonics and Advanced Instrument, Ministry of Education, Department of Physics, East China Normal University, Shanghai 200062, China

[a]happ1216@163.com, [b]htwnk@163.com, [c]wangxiaojun.2009@163.com, [d,*]hlli@phy.ecnu.edu.cn(Corresponding author), [e]zsun@phy.ecnu.edu.cn

Keywords: Sr_3SiO_5: Ce^{3+}, Li^+; Co-doping; Solid state method; Phosphor; LED

Abstract. This paper reports the spectral variation of Sr_3SiO_5: Ce^{3+}, Li^+ phosphor. It was synthesized by the conventional solid state method. The effects of calcining temperature and codoption of Mg^{2+} and Ba^{2+} on phase composition, structure, photoluminescence and thermal stability were firstly investigated in detail. Under the near-UV excitation of 415 nm, Sr_3SiO_5: Ce^{3+}, Li^+ emits a bright greenish-yellow color centered at 532nm, which originates from 5*d* to 4f ($^2F_{7/2}$ and $^2F_{5/2}$) transition of Ce^{3+}. The PL spectra show the different emission color variation with substituting Sr^{2+} cations with smaller Mg^{2+} or larger Ba^{2+}, which makes it be applied as a color-tunable phosphor for LED based on near-UV chip/phosphor technology. Simultaneously, the thermal stability of $(Sr,Ba)_3SiO_5$: Ce^{3+}, Li^+ phosphor is improved markedly.

Introduction

White light-emitting diodes (WLEDs) have been intensively studied due to their excellent properties such as low power consumption, friendly to environment, high reliability and long lifetime [1]. Several approaches can achieve the white light output by using LEDs structure [2,3]. Thereinto, the method by combining blue LED chips with yellow-emitting phosphor (YAG:Ce) was currently used and had been commercialized due to the low cost, high brightness and simple structure [4]. However, because the photoluminescence excitation (PLE) intensity of YAG:Ce is very weak in the near ultraviolet (n-UV) spectral region, YAG:Ce is not applicable to n-UV LED-pumped WLEDs.

Recently, Jang *et al.* reported Sr_3SiO_5: Ce^{3+},Li^+ phosphors that showed a strong and broad PLE band peaking at 415 nm, and thus white light can be generated from n-UV LEDs as well as blue LEDs by coating this phosphor onto these LED chips [5-7]. In addition, since the emission wavelength of Sr_3SiO_5: Ce^{3+},Li^+ can be adjusted by changing the amount of Ce^{3+}, the color temperature (T_c) and color rendering index (CRI) of Sr_3SiO_5: Ce^{3+},Li^+-based WLEDs can be controlled without mixing different kinds of phosphors [7]. Luo *et al.* found that the emission spectrum of Sr_3SiO_5: Ce^{3+} can also be tuned by changing the crystal field of Ce^{3+} through substitution of Si^{4+} with Al^{3+}, Ga^{3+} and B^{3+}, respectively [8]. Simultaneously, PL intensity was improved due to compensating charge imbalances between Ce^{3+} and Sr^{2+}. According to this result, optical properties of Sr_3SiO_5: Ce^{3+},Li^+ should be tailored when Sr^{2+} is replaced by different ion size of Mg^{2+} or Ba^{2+}.

In this work, Mg^{2+} or Ba^{2+}-codoped Sr_3SiO_5:Ce^{3+},Li^+ phosphors were prepared by the conventional solid-state method. The effects of calcining temperature and substitution of Sr^{2+} by Mg^{2+} and Ba^{2+} on the phase composition, structure and photoluminescent properties of the phosphor were investigated in detail. The spectra were optimized in order to explore phosphors with low T_c and high CRI for applications in near-UV white LEDs.

Experimental Procedure

Ba^{2+}, Mg^{2+} co-doped Sr_3SiO_5: Ce^{3+}, Li^+ phosphors were synthesized by the conventional solid-state method. Strontium carbonate, silicon oxide, cerium oxide, magnesium oxide, and barium carbonate were used as starting materials in the present work. Lithium carbonate was used as charge compensation. Silicate phosphors with compositions of $Sr_{2.94-x}M_xCe_{0.03}Li_{0.03}SiO_5$ (M=Mg and Ba, x=0.0—1.0) were prepared by weighing, mixing, and grinding the appropriate amount of starting materials in a mortar by hand. Subsequently, they were loaded into an alumina crucible and fired in an alumina tube furnace at 1200-1500℃ for 4 h under a reducing atmosphere (N_2:H_2=95:5).

X-ray powder diffraction (XRD) patterns of the synthesized phosphors were recorded on a D8 ADVANCE X-ray diffractometer. Photoluminescent (PL) spectra and Commission International del'Eclairge (CIE) chromaticity coordinates at RT were examined by a fluorescence spectrophotometer (Horiba Jobin Yvon, FluoroMax-4). To measure temperature-dependent luminescence of the phosphor, a high temperature fluorescence controller (TAP-02, Tianjin Orient KOJI Co., LTD.) was connected with the above-mentioned fluorescence spectrophotometer.

Results and Discussion

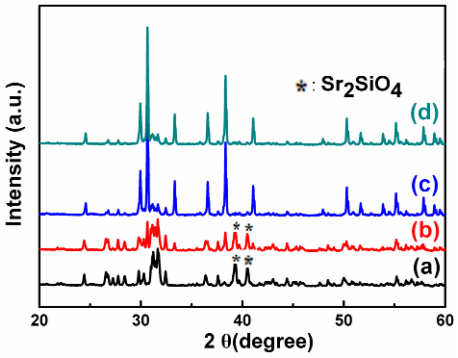

Fig. 1 XRD patterns of $Sr_{2.94}SiO_5$: Ce^{3+},Li^+ calcined at: (a) 1200℃, (b) 1300℃, (c) 1400℃, and (d) 1500℃.

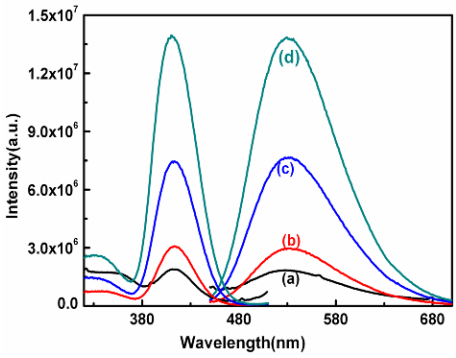

Fig. 2 The PLE and PL spectra of $Sr_{2.94}SiO_5$: Ce^{3+}, Li^+ calcined at: (a) 1200℃, (b) 1300℃, (c) 1400℃, (d) 1500℃.

Figure 1 shows XRD patterns of $Sr_{2.94}SiO_5$:0.03Ce^{3+}, 0.03Li^+ powders calcined at various temperatures for 4 h. It can be seen that the impurity phase of Sr_2SiO_4 can be observed except for the expected composition of Sr_3SiO_5 for the sample calcined at 1200℃ and 1300℃. Raising temperature to 1400 and 1500℃, the diffraction peaks of Sr_2SiO_4 decrease dramatically and nearly all of the diffraction peaks are consistence with the standard powder diffraction profile of Sr_3SiO_5 (JCPDS #18-1282).

Figure 2 shows the excitation and emission spectra of the $Sr_{2.94}SiO_5$: 0.03Ce^{3+}, 0.03Li^+ phosphors calcined at different temperatures. All samples give the similar excitation and emission spectra except for their emission intensities. The excitation spectra consist of two broad bands which ascribe to $4f \rightarrow {}^2D_{3/2}$ and $4f \rightarrow {}^2D_{5/2}$ transitions of Ce^{3+}. The excitation band ranges from approximately 300 to 500 nm and shows a strong intensity near at 415 nm. Under the excitation of 415 nm, $Sr_{2.94}SiO_5$: 0.03Ce^{3+}, 0.03Li^+ shows a strong broad emission centered at 532 nm. This greenish-yellow emission is attributed to the allowed transition from $5d$ to $4f$ ($^2F_{7/2}$ and $^2F_{5/2}$) of Ce^{3+} ions [9]. The luminescence of Ce^{3+} ions is strongly enhanced along with the increased calcination temperature. The intensity reaches the maximum at 1500℃, approximately 10 times higher than that of phosphor synthesized at 1200 ℃. The increased emission intensity can be ascribed to the growing of the crystalline.

Figure 3 shows the PL and PLE spectra of Sr_3SiO_5: Ce^{3+}, Li^+ phosphors with different substitution of Sr^{2+} by smaller Mg^{2+}. As seen, with increasing Mg content, the emission shifts toward shorter wavelength (i.e., 532 nm for x=0, and 517 nm for x=1.0). On the contrary, when Sr^{2+} in Sr_3SiO_5: Ce^{3+}, Li^+ is partially replaced by larger Ba^{2+}, the emission band at about 532 nm shifts to a longer

wavelength of 552 nm with an increase in Ba^{2+} concentration from x=0 to x=1.0, as shown in Fig. 4. This phenomenon (blueshift or redshift) can be explained in terms of the decreasing or increasing nephelnxetic effect [10]. With the decrease in the degree of covalence of Ce-O bonds in order of Ba, Sr, and Mg, less negative charges transfer to Ce^{3+} ions and thus increase the difference between the 4*f* and the 5*d* levels. So the degree of covalence in the Ce–O bonds is decreased with substitution of Sr ions with smaller Mg cations, and consequently can result in the blueshift of the Ce-O emission band (Fig. 3). Instead, the replacement of Sr^{2+} with larger Ba^{2+} leads to the degree of covalence in the Ce–O bonds increasing and the redshift of the Ce-O emission band (Fig. 4). Consequently, the emission color of Sr_3SiO_5: Ce^{3+}, Li^+ can be adjusted by partially replacement of Sr^{2+} with Mg^{2+} or Ba^{2+} , which make it apply to a variety of LEDs from blue LEDs (~ 450 nm chips) to n-UV LEDs (~ 410 nm chips).

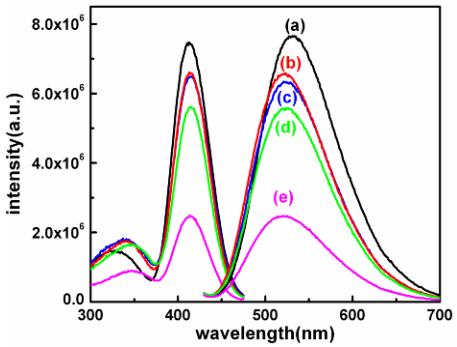

Fig. 3 The PL and PLE spectra of $Sr_{(2.94-x)}Mg_xSiO_5$: $0.03Ce^{3+}$, $0.03Li^{+}$: (a) x=0, (b) x=0.3, (c) x=0.5, (d) x=0.7, (e) x=1.0.

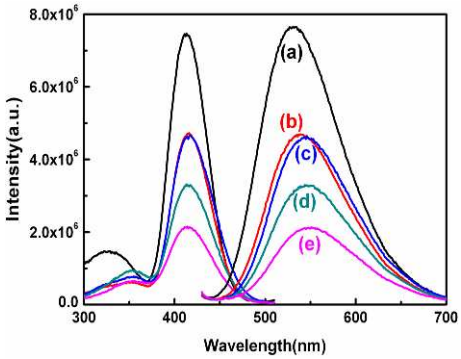

Fig. 4 The PL and PLE spectra of $Sr_{(2.94-x)}Ba_xSiO_5$: $0.03Ce^{3+}$,$0.03Li^{+}$: (a) x=0, (b) x=0.3, (c) x=0.5, (d) x=0.7, (e) x=1.0.

Generally, the most symmetrical structures give the least complicated diffraction patterns as the number of constituents in the crystal increases. It is indicated that phosphors, which are crystallized in the systems with the highest degree of symmetry, generally have the highest luminescence efficiency. The symmetry decreases with an increase of substitution of Sr^{2+} ions by Mg^{2+} or Ba^{2+} ions, thus, PL intensity accordingly decreases with an increase in Mg^{2+} or Ba^{2+} concentration, as shown in Figs. 3 and 4.

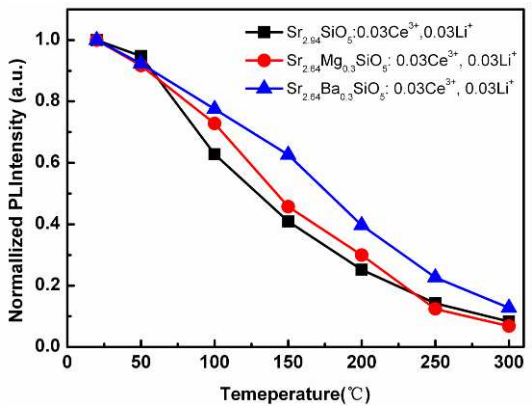

Fig. 5

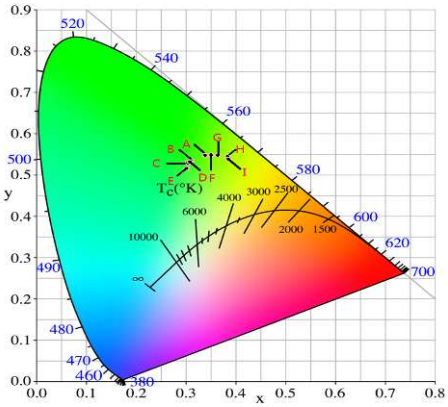

Fig. 6

Fig. 5 The temperature dependent emission intensity of $Sr_{2.94}SiO_5$:$0.03Ce^{3+}$,$0.03Li^{+}$, $Sr_{2.64}Mg_{0.03}SiO_5$: $0.03Ce^{3+}$, $0.03Li^{+}$, and $Sr_{2.64}Ba_{0.03}SiO_5$: $0.03Ce^{3+}$, $0.03Li^{+}$.

Fig. 6 CIE chromaticity points of $Sr_{2.94}SiO_5$: Ce^{3+},Li^{+} and different Mg or Ba codoped $Sr_{2.94}SiO_5$: Ce^{3+},Li^{+} phosphors : A–$Sr_{2.94}SiO_5$: Ce^{3+},Li^{+}, B–$Sr_{2.64}Mg_{0.3}SiO_5$: Ce^{3+},Li^{+}, C–$Sr_{2.44}Mg_{0.5}SiO_5$: Ce^{3+},Li^{+}, D–$Sr_{2.24}Mg_{0.7}SiO_5$: Ce^{3+},Li^{+}, E–$Sr_{1.94}MgSiO_5$: Ce^{3+},Li^{+}, F–$Sr_{2.64}Ba_{0.3}SiO_5$: Ce^{3+},Li^{+}, G–$Sr_{2.44}Ba_{0.5}SiO_5$: Ce^{3+},Li^{+}, H–$Sr_{2.24}Ba_{0.7}SiO_5$: Ce^{3+},Li^{+}, I–$Sr_{1.94}BaSiO_5$: Ce^{3+},Li^{+}.

The thermal stability of only Ce^{3+}, Li^{+}-doped Sr_3SiO_5 and Mg or Ba-codoped $Sr_{2.94}SiO_5$:0.03Ce^{3+},0.03Li^{+} phosphors was measured at 25-300℃, as illustrated in Fig. 5. One can find that the emission intensity of all samples decreases as the temperature rises, while the decreasing rate is different. The thermal quenching increases in order of Ba-doped, Mg-doped, and undoped $Sr_{2.94}SiO_5$:0.03Ce^{3+},0.03Li^{+}. At 150℃, where white LED usually work, the emission intensity of the undoped, Mg-codoped, and Ba-codoped samples remains 41%, 46%, and 63% , respectively, of that measured at 25℃. The thermal quenching can be explained by the temperature dependence of electron-phonon interactions in the luminescence center and thermally activated photo-ionization of lanthanide [11,12]. These two mechanisms are strongly related to the crystal structure of host lattices and the crystallinity of the phsophors [13]. It appears that the partially substitution with Ba^{2+} can markedly improve thermal stability of Sr_3SiO_5: Ce^{3+}, Li^{+} phosphor.

Figure 6 presents the CIE color coordinates of the chromaticity diagram. It can be found that the different color variation with substituting Sr^{2+} ctions with Mg^{2+} and Ba^{2+} cations. Only Ce^{3+},Li^{+}-doped Sr_3SiO_5 locates at greenish-yellow region in the chromaticity diagram. When Mg is gradually doped into the host lattice for Sr, the CIE coordinate shifts to the cyan region. Instead, for Ba codoped-sample, it shifts to yellow region. This phenomenon is consistent with the PL spectra in Figs. 3 and 4.

Conclusions

①Mg^{2+} or Ba^{2+} codoped Sr_3SiO_5: Ce^{3+}, Li^{+} phosphors were synthesized by a conventional solid state method. ②Under n-UV excitation, Sr_3SiO_5:Ce^{3+}, Li^{+} showed a greenish-yellow emission located at 532 nm. ③ The spectrum gave the corresponding blueshift (from 532 to 517 nm) or redshift (from 532 to 552 nm) when Sr^{2+} was partially replaced by smaller Mg^{2+} or larger Ba^{2+}, respectively. ④The substitution of Ba^{2+} for Sr^{2+} markedly improves thermal stability of Sr_3SiO_5: Ce^{3+}, Li^{+} phosphor. ⑤The as-prepared phosphors have a great potential for the solid state lighting based on n-UV LED chip.

References

[1] H. Y. Chen, M. H. Wen, R. Y . Yang and S. J. Chang: Ceram. Int. Vol. 37 (2011), P.1521.

[2] H. Wu, N. Narendran, Y. Gu and A. Bierman: *Improving the Performance of Miced-Color White LED Systems by Using Scattered Photon Extration Technique*, Seventh International Conference on Solid State Lighting Proceedings of SPIE, San Diego, CA, USA (2007).

[3] X. Y. Sun, L.W. Lin and W.F. Wang: Appl. Phys. A: Materials & Processing Vol. 104 (2011), P. 83.

[4] H. S. Jang, Y. H. Won and D. Y. Jeon: Appl. Phys. B: Lasers Opt. Vol. 95 (2009), P. 715.

[5] H. S. Jang, D. Y. Jeon: Opt. Lett.Vol. 32 (2007), P. 3444.

[6] C.Y. Shen and Y. Yang,: Opt. Mater. Vol. 250 (2009), P. 5230.

[7] H. S. Jang, H. Yang, S. W. Kim, J. Y. Han, S. G. Lee and D. Y. Jeon,: Adv. Mater. Vol.20 (2008), P.1.

[8] H. Luo, J. Liu, X. Zheng, L. Han, K. Ren and X. Yu: J. Mater. Chem. Vol. 22 (2012), P.15887.

[9] H. S. Janga and D. Y. Jeonl: Appl. Phys. Lett. Vol. 90 (2007), P.041906.

[10] J. S. Kim, P. E. Jeon, J. C. Choi and H. L. Park: Solid State Commun. Vol.133 (2005), P.187.

[11] V. B. Mikhailik, H. Kraus, D. Wahl, M. Itoh, M. Koike and I. K. Bailiff: Phys. Rev. B: Condens. Matter Mater. Phys. Vol. 69 (2004), P.205110.

[12] E. van der Kolk, P. Dorenbos, J. T. M. de Haas and C. W. E. van Eijk: Phys. Rev. B: Condens. Matter Mater. Phys. Vol.**71** (2005), P.045121.

[13] M. Ando and Y. A. Ono: J. Cryst. Growth Vol. 117 (1992), P.969.