Article ID: 1000-7032(2010)01-0049-05

Luminescence Characteristics of $LiCaBO_3:Sm^{3+}$ Phosphor

WANG Zhi-jun[1], LIU Hai-yan[2], ZHANG Kun[2],
YANG Zhi-ping[1], GUO Qing-lin[1], LI Pan-lai[1]*, LI Xu[1], YANG Yan-min[1]

(1. *College of Physics Science & Technology, Hebei University, Baoding* 071002, *China*;
2. *Industrial & Commercial College, Hebei University, Baoding* 071002, *China*)

Abstract: $LiCaBO_3:Sm^{3+}$ phosphor was synthesized by solid state reaction and its luminescent properties were studied. The emission spectrum consists of three major orange-red emission bands at 561, 602 and 651 nm, which correspond to the $^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^4G_{5/2}\rightarrow{}^6H_{7/2}$ and $^4G_{5/2}\rightarrow{}^6H_{9/2}$ typical transitions of Sm^{3+}, respectively. The excitation spectrum for the strongest emission (602 nm) extends in 320~420 nm, which indicated that this phosphor can be effectively excited by near-ultraviolet light-emitting diodes. The influences of Sm^{3+} concentration (x) on the emission intensity of $LiCa_{1-x}BO_3:xSm^{3+}$ phosphors were also investigated. The results showed that the intensity increases with increasing Sm^{3+} concentration, then decreases, and reaches the maximal value at 3% Sm^{3+}. And the concentration self-quenching mechanism is the d-d interaction according to Dexter theory. The emission intensity of $LiCaBO_3:Sm^{3+}$ can be enhanced by doping charge compensator Li^+, Na^+, K^+.

Key words: luminescence; borate; Sm^{3+}

CLC number: O482.31 **PACS**: 78.55.Hx **PACC**: 3250F; 7855 **Document code**: A

1 Introduction

Recently, the luminescence capabilities of GaN chips under the range of near ultraviolet (UV) (350~410 nm) have increased, and so the white LEDs excited by UV chips have become an important focus research[1~7]. Because the eyes are insensitive to radiation in the range of 350~410 nm, the color of this white LEDs depends completely on phosphor. The kind of phosphors and the mixture ratio can be varied to adjust the chromaticity of the illuminating source according to different needs. Consequently, optical conversion materials for the UV LED have obtained extensively attention, and the emission spectrum of these materials is an important index which can scale the capability of the materials. At present, there are a few reports about green and blue phosphors excited by UV LED chips[8~10]. However, there have been few reports about red phosphor. Alkaline earth borate is an important luminescent material because of its excellent chemistry and thermal stability, facile synthesis and cheap raw material (H_3BO_3), so it has been extensively applied in phosphor for lamps. In the present work, $LiCaBO_3:Sm^{3+}$ red phosphor was synthesized and investigated. The results could help the development of white-emitting LED.

2 Experiments

2.1 Preparation

$LiCaBO_3:Sm^{3+}$ samples were prepared by solid-state reaction. The starting materials are the analytical reagents $CaCO_3$, H_3BO_3, Li_2CO_3, Na_2CO_3, K_2CO_3 and Sm_2O_3 (99.99% in mass). After the individual materials were mixed in the requisite proportions sufficiently, the powders were calcined at

Received date: 2009-04-01; **Revised date**: 2009-06-02
Foundation item: Project supported by the National Natural Science Foundation of China (50902042); the Natural Science Foundation of Hebei Province (E2009000209); the Education Office Foundation of Hebei Province (2009313)
Biography: WANG Zhi-jun, born in 1979, female, Hebei Province. Her work focuses on luminescence materials.
E-mail: wangzhijunmail@yahoo.com.cn, Tel: (0312)5079423
*: Corresponding Author; E-mail: lipanlai@sohu.com

700 ℃ for 2 h. The obtained products are $LiCaBO_3$: Sm^{3+} phosphors.

2.2 Measurement

The structure was checked by powder XRD(D/max-rA, Cu Kα, 40 kV, 100 mA). The emission and excitation spectra were measured by Shimadzu RF-540 fluorescence spectrophotometer. All the photoluminescence properties of the phosphors were measured at room temperature.

3 Results and Discussion

3.1 Structure of $LiCaBO_3$: Sm^{3+} Phosphor

The XRD pattern of $LiCaBO_3$: Sm^{3+} phosphor with mole fraction 1% Sm^{3+} is shown in Fig. 1 and it agrees well with references [11,12], indicating that the doped Sm^{3+} have not caused any significant change in the host structure. $LiCaBO_3$ has an orthorhombic structure with *Pbca* space group, and its lattice parameters are $a = 1.322\ 7$ nm, $b = 0.616\ 75$ nm, $c = 0.606\ 20$ nm.

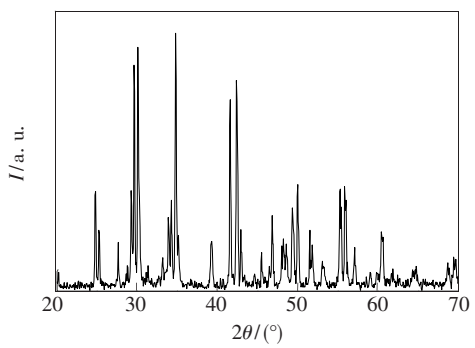

Fig. 1 XRD pattern of $LiCaBO_3$: Sm^{3+} phosphor

3.2 Emission and Excitation Spectra of the $LiCaBO_3$: Sm^{3+} Phosphor

Fig. 2 shows both the emission and excitation spectra of $LiCaBO_3$: Sm^{3+} phosphor with 1% Sm^{3+}. Under 365 nm excitation, $LiCaBO_3$: Sm^{3+} phosphor exhibits three major orange-red emission bands at 561, 602 and 651 nm, which correspond to the $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$ and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ typical transitions of Sm^{3+}, respectively. The strongest one appears at 602 nm. The three typical emission peaks are split in different ways. The energy level transition $^4G_{5/2} \rightarrow {}^6H_{5/2}$ is split into 561 and 567 nm emission peaks; $^4G_{5/2} \rightarrow {}^6H_{7/2}$ is split into 602 and 611 nm emission peaks, and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ is split into 651 and 659 nm emission peaks. These splits are resulted from the crystal field effects, and their extents are related to the structure characteristic of $LiCaBO_3$ crystal field. The excitation spectrum for 602 nm emission has several bands at 347, 374 and 406 nm, which correspond to the characteristic f-f transitions of Sm^{3+}. The strongest one is at 406 nm, which is attributed to the $^6H_{5/2} \rightarrow {}^4L_{13/2}$ transition of Sm^{3+}.

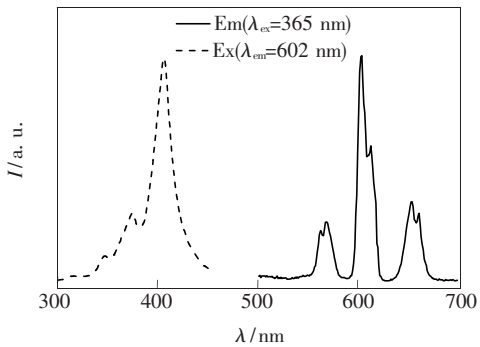

Fig. 2 Emission and excitation spectra of $LiCaBO_3$: Sm^{3+} phosphor. Emission spectrum consists of three major orange-red emission bands at 561, 602 and 651 nm, and excitation spectrum for 602 nm extends in 320 ~ 420 nm.

3.3 Effect of Sm^{3+} Concentration on Emission Intensity of $LiCaBO_3$: Sm^{3+} Phosphor

A variety of samples with different Sm^{3+} concentrations (x) were synthesized, and the effects of Sm^{3+} concentration on the emission intensities of $LiCa_{1-x}BO_3$: xSm^{3+} phosphors were also investigated. The Sm^{3+} concentration is varied in 1% ~6%, and the emission intensity with different Sm^{3+} concentrations is displayed in Fig. 3. The results show that the emission intensity is influenced by Sm^{3+} concentrations. At low Sm^{3+} concentrations ($x < 3\%$), the luminescence center is not sufficient and the emission intensity is weak. The emission intensity increases with increasing Sm^{3+} concentration, and reaches the maximum at 3% Sm^{3+}. Concentration quenching occurs when the Sm^{3+} concentration is beyond 3%. The reason for the concentration quenching is that, as the concentration of Sm^{3+} increases, the probability of Sm^{3+}-Sm^{3+} interaction increases, leading to the emission intensity decreases.

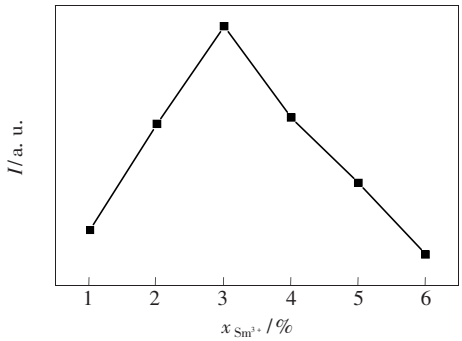

Fig. 3　Emission intensity of $LiCa_{1-x}BO_3:xSm^{3+}$ phosphor as function of Sm^{3+} concentration. Firstly, the emission intensity increases with increasing Sm^{3+} concentration, and reaches the maximum at 3% Sm^{3+}, and then decreases.

Dexter [13] proposed that the interaction type between sensitizers and activator can be determined by $\lg(I/x) = c - (\theta/3)\lg x$ when the concentration is high enough. Among the concentration quenching caused by the electric multipole interaction, the dipole-dipole (d-d), dipole-quadripole (d-q) and quadripole-quadripole (q-q) correspond to $\theta = 6$, 8, 10, respectively. According to the method, the emission intensity of $LiCa_{1-x}BO_3:xSm^{3+}$ phosphor is measured under the condition that Sm^{3+} concentration is 3%, 4%, 5%, 6%, the concentration dependence curve [$\lg(I/x)$-$\lg x$] is shown in Fig. 4. From the slope of the linear, we can obtain $\theta = 5.98 \approx 6$. The result indicates that the concentration self-quenching mechanism of Sm^{3+} in $LiCaBO_3$ is the d-d interaction.

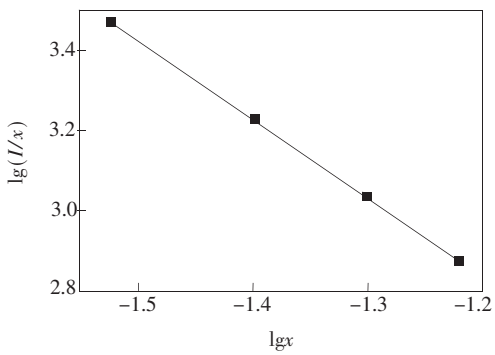

Fig. 4　Relation between the $\lg(I/x)$ and $\lg x$ of Sm^{3+}

3.4　Effect of Charge Compensator on Emission Spectra of $LiCaBO_3:Sm^{3+}$ Phosphor

When a trivalent metallic ion, such as Sm^{3+}, is incorporated into a host lattice and substitutes for a divalent metallic ion, the charge balancing is necessarily required. For $LiCa_{1-x}BO_3:xSm^{3+}$, Ca^{2+} is substituted by Sm^{3+}, and should produce positive univalent charge surplus; when Ca^{2+} is substituted by Li^+, Na^+ or K^+, should produce negative charge univalent surplus, the whole presents electricity neutrality due to the attraction of particles with opposite charges. Consequently, we dope Li^+, Na^+ or K^+ into $LiCa_{1-x}BO_3:xSm^{3+}$, and investigate the emission spectra of $LiCa_{1-x}BO_3:xSm^{3+}$ phosphor. Li^+, Na^+ or K^+ concentration (y) are all in the range of 1% ~ 6%, and x is 3% in this research. Under the condition of doping Li^+, the influence of Li^+ concentrations on the emission spectra of $LiCa_{1-x-y}BO_3:xSm^{3+},yLi^+$ phosphor is observed, and the result is shown in Fig. 5. The results show that the emission intensity increases with increasing Li^+ concentration, and reaches the maximal value at 4% Li^+ then decreases. Under the condition that Na^+ or K^+ is introduced, the same results can be obtained. However, the charge compensator concentration corresponding to the maximum is different with different charge compensator, and the concentration is 4% and 3% corresponding to Na^+ and K^+, respectively. We compared with the maximal emission intensity with doping Li^+, Na^+ and K^+, as shown is Fig. 6. And the results show that the maximal emission intensity of doping Li^+ is higher than that of Na^+ or K^+, the result is well agreement with the Ref. [14].

The results can be explained by the following reasons: when the charge compensator is incorporated into a host lattice, the aberration is brought in

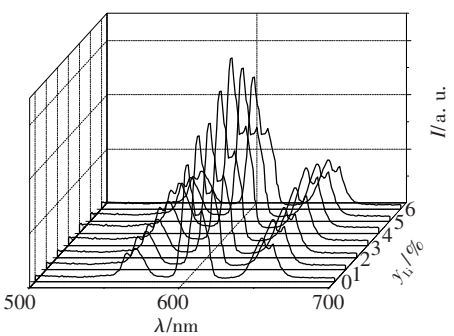

Fig. 5　Emission spectra of $LiCa_{1-x-y}BO_3:xSm^{3+},yLi^+$ phosphor as function of Li^+ concentration.

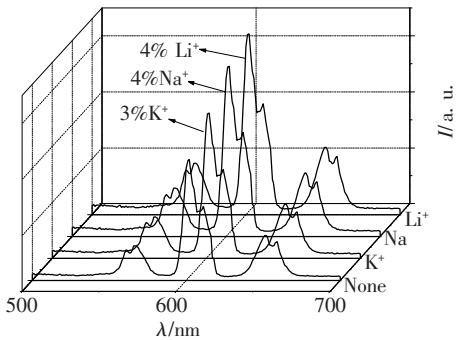

Fig. 6 Effect of Li^+, Na^+ and K^+ on emission spectra of $LiCa_{1-x-y}BO_3: xSm^{3+}, yN$ ($N = Li^+$, Na^+, K^+) phosphor.

the crystal lattice, which would induce the probability change of transition emission and enhance the emission intensity of $LiCa_{1-x-y}BO_3: xSm^{3+}, yLi^+$ phosphor. However, the emission intensity does not increase all along with increasing charge compensator concentration. This means that only portion charge compensator is incorporated into a host lattice, when the doping concentration is higher than the Sm^{3+} concentration, the excrescent part will substitute for the Ca^{2+} site, and the excrescent negative charge should make the emission intensity decreases[15].

The difference of ionic radius can be used to explain that the charge compensator concentration corresponding to the maximal emission intensity is different with different charges. The radius of Ca^{2+} in the host lattice is 0.118 nm, and the radii of Li^+, Na^+ and K^+ are 0.059, 0.116 and 0.133 nm, respectively. K^+, Li^+ and Na^+ are easily incorporated into the host lattice.

4 Conclusion

In summary, $LiCaBO_3: Sm^{3+}$ phosphor is synthesized by solid state reaction. The emission and excitation spectra show that this phosphor can be efficiently excited by ultraviolet LED, and emits 602 nm red light. The emission intensity of $LiCaBO_3: Sm^{3+}$ phosphor increases with increasing Sm^{3+} concentration, and reaches the maximal value at 3% Sm^{3+}, then decreases. The concentration self-quenching mechanism is the d-d interaction according to Dexter theory. The emission intensity of $LiCa_{1-x-y}BO_3: xSm^{3+}, yLi^+$ is enhanced by doping charge compensator Li^+, Na^+, K^+. Therefore, $LiCaBO_3: Sm^{3+}$ phosphor is an appropriate red-emitting phosphor for white LEDs.

References:

[1] Kim J S, Jeon P E, Choi J C, *et al.* Warm-white-light emitting diode utilizing a single-phase full-color $Ba_3MgSi_2O_8: Eu^{2+}$, Mn^{2+} phosphor [J]. *Appl. Phys. Lett.*, 2004, **84**(15):2931-2933.

[2] Park J K, Lim M A, Kim C H, *et al.* White light-emitting diodes of GaN-based Sr_2SiO_4: Eu and the luminescent properties [J]. *Appl. Phys. Lett.*, 2003, **82**(5):683-685.

[3] Yang Zhiping, Wang Shaoli, Yang Guangwei, *et al.* Preparation and luminescent properties of green $NaCaPO_4: Tb^{3+}$ phosphor [J]. *Chin. J. Lumin.* (发光学报), 2008, **29**(1):71-74 (in Chinese).

[4] Sun Xiaoyuan, Zhang Jiahua, Zhang Xia, *et al.* A single white phosphor suitable for near ultraviolet excitation applied to new generation white LED lighting [J]. *Chin. J. Lumin.* (发光学报), 2005, **26**(3):404-406 (in Chinese).

[5] Li Xu, Yang Yong, Yang Zhiping, *et al.* Fabrication and properties of Eu^{3+} doped $La_2Mo_2O_9$ red phosphor [J]. *Chin. J. Lumin.* (发光学报), 2008, **29**(1):93-96 (in Chinese).

[6] Yang Yi, Jin Shangzhong, Shen Changyu, *et al.* Spectral properties of alkaline earth composite silicate phosphors for white LED [J]. *Chin. J. Lumin.* (发光学报), 2008, **29**(5):800-804 (in Chinese).

[7] Li Xuzheng, Wang Dajian, Gu Tiecheng, *et al.* Sol spray-microwave cancining and luminescent properties of $Ba_2MgSi_2O_8$ hosted phosphors for white light emitting diodes [J]. *Chin. J. Lumin.* (发光学报), 2008, **29**(6):989-995 (in Chinese).

[8] Park J K, Lim M A, Choi K J, *et al.* Luminescence characteristics of yellow emitting $Ba_3SiO_5: Eu^{2+}$ phosphor [J]. *J. Mater. Sci.*, 2005, **40**(8):2069-2071.

[9] Lim M A, Park J K, Kim C H, *et al.* Luminescence characteristics of green light emitting $Ba_2SiO_4: Eu^{2+}$ phosphor [J].

J. Mater. Sci. Lett., 2003, **22**(19):1351-1353.

[10] Yang Zhiping, Zhao Fangliang, Li Xiaoning, *et al.* Luminescent properties of $Sr_3B_2O_6:Tb^{3+}$, Li^+ green phosphor [J]. *Chin. J. Lumin.* (发光学报), 2008, **29**(6):941-944 (in English).

[11] Wu L, Chen X L, Li H, *et al.* Structure determination of a new compound $LiCaBO_3$ [J]. *J. Solid State Chemistry*, 2004, **177**(4-5):1111-1116.

[12] Jiang L H, Zhang Y L, Li C Y, *et al.* Thermoluminescence characteristics of rare-earth-doped $LiCaBO_3$ phosphor [J]. *J. Lumin.*, 2008, **128**(12):1904-1908.

[13] Dexter D L, Schulman J H. Concentration and excitation efffects in multiphonon non-radiative transitions of rare-earth ions [J]. *J. Chem. Phys.*, 1954, **22**(5):1063-1067.

[14] Yu X B, Xu X L, Zhou C L, *et al.* Synthesis and luminescent properties of $SrZnO_2:Eu^{3+}$, M^+ (M = Li, Na, K) phosphor [J]. *Materials Research Bulletin*, 2006, **41**(8):1578-1583.

[15] Tian L H, Mho S I. Enhanced luminescence of $SrTiO_3:Pr^{3+}$ by incorporation of Li^+ ion [J]. *Solid State Communications*, 2003, **125**(11-12):647-651.

$LiCaBO_3:Sm^{3+}$ 材料的发光特性

王志军[1], 刘海燕[2], 张　坤[2], 杨志平[1],
郭庆林[1], 李盼来[1*], 李　旭[1], 杨艳民[1]

(1. 河北大学 物理科学与技术学院, 河北 保定　071002; 2. 河北大学 工商学院, 河北 保定　071002)

摘要: 以 $CaCO_3$(99.9%)、Li_2CO_3(99.9%)、Na_2CO_3(99.9%) K_2CO_3(99.9%)、H_3BO_3(99.9%)、Sm_2O_3(99.9%)为原料,按所设计的化学计量比称取以上原料,在玛瑙研钵中混合均匀并充分研磨,装入刚玉坩埚,采用固相法制备 $LiCaBO_3:Sm^{3+}$ 材料;通过美国 XRD6000 型 X 射线衍射仪和日本岛津 RF-540 荧光分光光度计对材料的性能进行表征,所有测量均在室温条件下进行。$LiCaBO_3:Sm^{3+}$ 材料的发射光谱由三个橙红色发射峰组成,主峰位于 561,602,651 nm,分别对应 Sm^{3+} 的 $^4G_{5/2}\rightarrow{}^6H_{5/2}$、$^4G_{5/2}\rightarrow{}^6H_{7/2}$ 和 $^4G_{5/2}\rightarrow{}^6H_{9/2}$ 跃迁;监测 602 nm 发射峰,得到其激发光谱由 320~420 nm 的宽激发带组成。由激发和发射光谱看出,$LiCaBO_3:Sm^{3+}$ 能够有效地被紫外 LED 芯片激发,发射红色光。研究了 Sm^{3+} 浓度(x)对 $LiCa_{1-x}BO_3:xSm^{3+}$ 材料发射强度的影响,结果表明:随 Sm^{3+} 浓度的增大,发射强度先增强后减弱,Sm^{3+} 掺杂摩尔分数为 3% 时,发射强度最大,依据 Dexter 理论,计算得出其浓度猝灭机理为电偶极-偶极相互作用。掺入电荷补偿剂 Li^+、Na^+ 和 K^+ 均提高了 $LiCaBO_3:Sm^{3+}$ 材料的发射强度。

关　键　词: 发光; 硼酸盐; 三价钐离子
中图分类号: O482.31　　**PACS:** 78.55.Hx　　**PACC:** 3250F; 7855　　**文献标识码:** A
文章编号: 1000-7032(2010)01-0049-05

收稿日期: 2009-04-01; **修订日期:** 2009-06-02
基金项目: 国家自然科学基金(50902042); 河北省自然科学基金(E2009000209); 河北省教育厅基金(2009313)资助项目
作者简介: 王志军(1979-), 女, 河北沧州人, 主要从事发光材料方面的研究。
E-mail: wangzhijunmail@yahoo.com.cn, Tel: (0312)5079423
*: 通讯联系人; E-mail: lipanlai@sohu.com