

A novel white-bluish emitting phosphor of $(\text{Ba}_{0.49}\text{Sr}_{0.49})_2\text{B}_2\text{P}_2\text{O}_{10}:0.02\text{Eu}^{2+}$ for white LEDs*

PANG Li-bin (庞立斌)^{1,2**}, GAO Shao-jie (高少杰)¹, GAO Zhan-jun (高占军)¹, LI Hong-lian (李红莲)³, and WANG Zhi-jun (王志军)^{2**}

1. Department of Foreign Language Teaching and Research, Hebei University, Baoding 071002, China

2. College of Physics Science & Technology, Hebei University, Baoding 071002, China

3. College of Quality & Technical Supervision, Hebei University, Baoding 071002, China

(Received 26 February 2013)

©Tianjin University of Technology and Springer-Verlag Berlin Heidelberg 2013

A novel white-bluish emitting phosphor of $(\text{Ba}_{0.49}\text{Sr}_{0.49})_2\text{B}_2\text{P}_2\text{O}_{10}:0.02\text{Eu}^{2+}$ is synthesized by the solid state reaction. $(\text{Ba}_{0.49}\text{Sr}_{0.49})_2\text{B}_2\text{P}_2\text{O}_{10}:0.02\text{Eu}^{2+}$ can be effectively excited by 370 nm ultraviolet (UV) light, and exhibits two emission bands at 430 nm and 522 nm which are attributed to the d-f transitions of the Eu^{2+} ions in two different cation sites in the host lattices. And the chromaticity coordinate of $(\text{Ba}_{0.49}\text{Sr}_{0.49})_2\text{B}_2\text{P}_2\text{O}_{10}:0.02\text{Eu}^{2+}$ phosphor is (0.29, 0.25).

Document code: A **Article ID:** 1673-1905(2013)04-0282-3

DOI 10.1007/s11801-013-3032-4

The combination of red, green and blue phosphors with ultraviolet (UV) or near-UV (350–410 nm) light-emitting diodes (LEDs) is a common method for the generation of white light. However, in the method, the blue emission efficiency is poor because of the strong reabsorption of the blue light by the red or green emitting phosphors. Therefore, many effects^[1-8] have been made to develop the single-phase white-emitting phosphors based on the energy transfers from Eu^{2+} to Mn^{2+} , from Ce^{3+} to Eu^{2+} , from Ce^{3+} to Mn^{2+} and from Ce^{3+} to Tb^{3+} . Moreover, singly doping Eu^{2+} , Eu^{3+} or Dy^{3+} can also obtain the white light emitting phosphor^[9-11]. Besides, the emission intensity and wavelength of the phosphors would be affected and tuned by the concentration of the activator during changing the local surroundings around Eu^{2+} sites by varying Eu^{2+} and M^{2+} ($\text{M}=\text{Ca}$, Sr , Ba) concentrations^[12-14].

In the last decade, many novel Eu^{2+} and Mn^{2+} co-doped borophosphates were reported and structurally characterized^[15,16]. These studies revealed that the Eu^{2+} doped borophosphates could be a kind of photoluminescent materials with high efficiency. The absorption and emission bands of activators Eu^{2+} can also be well controlled by varying the crystal field or the bond covalence which depends on site size, site symmetry and coordination environment of activator ions^[17,18]. $\text{Ba}_2\text{B}_2\text{P}_2\text{O}_{10}$ and $\text{Sr}_2\text{B}_2\text{P}_2\text{O}_{10}$ are both luminescence hosts with the stable crystal structure and high thermal stability. Ba^{2+} and Sr^{2+} ions occupy two different coordinated sites with a different R-O distance. In this paper, in order to obtain the single white light emitting phosphor, $(\text{Ba}, \text{Sr})_2\text{B}_2\text{P}_2\text{O}_{10}:\text{Eu}^{2+}$ phosphors

are synthesized, and the color variations of emission attributed to the two emission bands of Eu^{2+} are also discussed from the perspective of crystal field strength and the covalence of hosts. White phosphor-converted (pc) LEDs are also fabricated by the combination of 370 nm LED chips and the as-synthesized phosphors.

$(\text{Ba}_{1-x-y}\text{Sr}_y)_2\text{B}_2\text{P}_2\text{O}_{10}:\text{xEu}^{2+}$ was synthesized by the solid state reaction. SrCO_3 , BaCO_3 , H_3BO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$ and Eu_2O_3 were used as the starting materials. After these materials were ground thoroughly in an agate mortar respectively, the homogeneous mixture was heated at 1000 °C for 5 h in a reducing atmosphere with 5% H_2 and 95% N_2 , and then these phosphors were obtained.

The present phase of the samples was characterized by powder X-ray diffraction (XRD) ($\text{D}/\text{max-rA}$, $\text{Cu K}\alpha$, 40 kV, 40 mA, $\lambda=0.15406$ nm). The emission and excitation spectra were measured by a SHIMADZU RF-540 fluorescence spectrophotometer. The commission international de l'Eclairage (CIE) chromaticity coordinates of the phosphors were measured by a PMS-80 UV-VIS-near IR spectrophotometer. All properties of the samples were studied at room temperature.

The XRD patterns of $\text{Ba}_2\text{B}_2\text{P}_2\text{O}_{10}$ (JCPDS No.19-0096), $\text{Sr}_2\text{B}_2\text{P}_2\text{O}_{10}$ (JCPDS No.18-1270) and the optimized phosphors of $(\text{Ba}_{1-x-y}\text{Sr}_y)_2\text{B}_2\text{P}_2\text{O}_{10}:\text{xEu}^{2+}$ ($x=0.02$, $y=0.01$, 0.3 , 0.49 and 0.98) are shown in Fig.1. Among all $(\text{Ba}, \text{Sr})_2\text{B}_2\text{P}_2\text{O}_{10}:\text{Eu}^{2+}$ phases, only $\text{Ba}_2\text{B}_2\text{P}_2\text{O}_{10}:0.02\text{Eu}^{2+}$ and $\text{Sr}_2\text{B}_2\text{P}_2\text{O}_{10}:0.02\text{Eu}^{2+}$ are obtained as a single phase, whereas other analogues are the mixtures of the known phases which belong to the $\text{Ba}_2\text{B}_2\text{P}_2\text{O}_{10}$ and $\text{Sr}_2\text{B}_2\text{P}_2\text{O}_{10}$, respectively.

* This work has been supported by the Natural Science Foundation of Hebei Province in China (No.D2012201115).

** E-mails: lizhibin268@sohu.com; wangzhijunmail@yahoo.com.cn

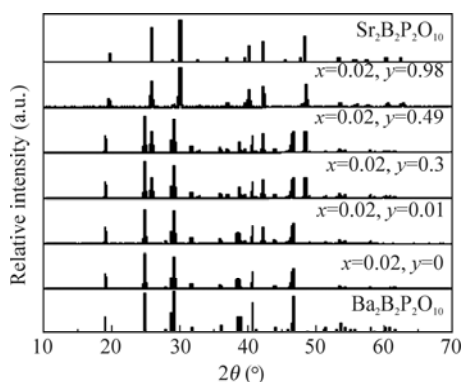


Fig.1 XRD patterns of $\text{Ba}_2\text{B}_2\text{P}_2\text{O}_{10}$ (JCPDS No.19-0096), $\text{Sr}_2\text{B}_2\text{P}_2\text{O}_{10}$ (JCPDS No.18-1270) and $(\text{Ba}_{1-x}\text{Sr}_y)_2\text{B}_2\text{P}_2\text{O}_{10}:\text{xEu}^{2+}$ ($x=0.02$, $y=0, 0.01, 0.3, 0.49$ and 0.98)

Fig.2 shows the emission spectra of $(\text{Ba}_{1-x}\text{Sr}_y)_2\text{B}_2\text{P}_2\text{O}_{10}:\text{xEu}^{2+}$ ($x=0.02$, $y=0.01, 0.3, 0.49$ and 0.98) and the excitation spectra of $\text{Ba}_2\text{B}_2\text{P}_2\text{O}_{10}:\text{Eu}^{2+}$ and $\text{Sr}_2\text{B}_2\text{P}_2\text{O}_{10}:\text{Eu}^{2+}$. The asymmetry emission of Eu^{2+} in $\text{Ba}_2\text{B}_2\text{P}_2\text{O}_{10}$ and $\text{Sr}_2\text{B}_2\text{P}_2\text{O}_{10}$ can be considered as a superposition of two Gaussian components. According to Ref.[19], the spectrum of $\text{Sr}_2\text{B}_2\text{P}_2\text{O}_{10}:\text{Eu}^{2+}$ phosphor consists of two peaks at 430 nm and 490 nm which come from Eu^{2+} substitute for Sr sites (Sr1 and Sr2), and that of $\text{Ba}_2\text{B}_2\text{P}_2\text{O}_{10}:\text{Eu}^{2+}$ contains 514 nm (Ba1) and 560 nm (Ba2), respectively. With the substitution of Ba^{2+} for Sr^{2+} (i.e., from $\text{Ba}_2\text{B}_2\text{P}_2\text{O}_{10}:\text{Eu}^{2+}$ to $\text{Sr}_2\text{B}_2\text{P}_2\text{O}_{10}:\text{Eu}^{2+}$), the emission bands of longer wavelength show a blue shift, whereas these of shorter wavelength show a red shift.

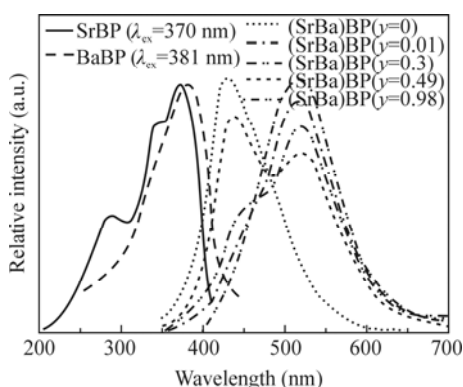


Fig.2 Emission and excitation spectra of $(\text{Ba}_{1-x}\text{Sr}_y)_2\text{B}_2\text{P}_2\text{O}_{10}:\text{xEu}^{2+}$ ($x=0.02$, $y=0, 0.01, 0.3, 0.49$ and 0.98) phosphors

These results could be explained in terms of two competing factors: the crystal field and the bond covalence. The crystal field strength increases with decreasing bond length by replacing Ba^{2+} with smaller Sr^{2+} cations. The correlation between the crystal field strength and bond length is given as^[20]

$$D_q = 3Ze^2r^4/5R^5, \quad (1)$$

where D_q is the crystal field strength, R is the bond

length between a center ion and ligands, r is the mean size of a center ion, and Z is the charge of a center ion. Therefore, the increase of the crystal field strength could result in a red shift for 5d-4f transition of Eu^{2+} , as reported by Kim *et al*^[20]. In addition, the observed blue shift can be attributed to the decreasing nephelauxetic effect^[21]. With the decreasing degree of covalence in Eu-O bands (in the other Ba and Sr), less negative charges transfer to Eu^{2+} ions, and thus the energy difference between the 4f and the 5d levels is increased. Thus, the degree of covalence in the Eu-O bonds is decreased with the substitution of Ba^{2+} for smaller Sr^{2+} cations, so the blue shift of the Eu^{2+} emission band is introduced.

In the case of $\text{Ba}_2\text{B}_2\text{P}_2\text{O}_{10}:\text{Eu}^{2+}$ to $\text{Sr}_2\text{B}_2\text{P}_2\text{O}_{10}:\text{Eu}^{2+}$, the size difference between the M(2) site and ionic radius of Eu^{2+} is too much larger than that between M(1) site and ionic radius of Eu^{2+} ion. The symmetry of ligand ions around Eu^{2+} ions is slightly distorted, and their crystal fields are relaxed. The ligand ions should not effectively exert the crystal field on Eu^{2+} ions occupying the M(2) sites. Consequently, the bond covalence effect in M(2) site is dominant, and the covalence decreases in order of $\text{Ba}^{2+} > \text{Sr}^{2+}$, so that the slight blue shift of Eu^{2+} (2) emission at longer wavelength is observed. On the other hand, the difference between the size of M(1) site and ionic radius of Eu^{2+} ions is smaller than that between the size of M(2) site and ionic radius of Eu^{2+} ions. The Eu^{2+} ions occupying the larger M(1) site are dominantly affected by the crystal field, which causes the slight red shift of Eu^{2+} (1) emission at shorter wavelength.

Fig.3 shows the commission international de l'Eclairage (CIE) chromaticity diagram with empirical CIE coordinates under excitation at 370 nm. The chromaticity coordinates of optimized phosphors of $(\text{Ba}_{0.97}\text{Sr}_{0.01})_2\text{B}_2\text{P}_2\text{O}_{10}:0.02\text{Eu}^{2+}$, $(\text{Ba}_{0.68}\text{Sr}_{0.3})_2\text{B}_2\text{P}_2\text{O}_{10}:0.02\text{Eu}^{2+}$ and $(\text{Ba}_{0.49}\text{Sr}_{0.49})_2\text{B}_2\text{P}_2\text{O}_{10}:0.02\text{Eu}^{2+}$ are (0.21, 0.31), (0.23, 0.25) and (0.29, 0.25), respectively. The inset shows the photograph of bluish-white $(\text{Ba}_{0.49}\text{Sr}_{0.49})_2\text{B}_2\text{P}_2\text{O}_{10}:0.02\text{Eu}^{2+}$ phosphor under the 365 nm excitation.

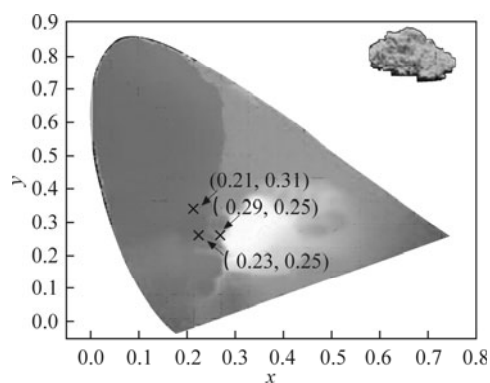


Fig.3 CIE chromaticity diagram for $(\text{Ba}_{0.97}\text{Sr}_{0.01})_2\text{B}_2\text{P}_2\text{O}_{10}:0.02\text{Eu}^{2+}$, $(\text{Ba}_{0.68}\text{Sr}_{0.3})_2\text{B}_2\text{P}_2\text{O}_{10}:0.02\text{Eu}^{2+}$ and $(\text{Ba}_{0.49}\text{Sr}_{0.49})_2\text{B}_2\text{P}_2\text{O}_{10}:0.02\text{Eu}^{2+}$ excited at 370 nm (The inset shows the $(\text{Ba}_{0.49}\text{Sr}_{0.49})_2\text{B}_2\text{P}_2\text{O}_{10}:0.02\text{Eu}^{2+}$ photo taken under 365 nm excitation in a UV box.)

In summary, $(\text{Ba}_{1-x-y}\text{Sr}_y)_2\text{B}_2\text{P}_2\text{O}_{10}:x\text{Eu}^{2+}$ phosphors are synthesized by a conventional solid state reaction. The phosphors can be effectively excited by 370 nm light, and exhibit two emission bands which are attributed to the f-d transitions of doped Eu^{2+} ions in two different cation sites in host lattices, and color variation of emission is observed by substituting the M^{2+} sites. And the chromaticity coordinate of $(\text{Ba}_{0.49}\text{Sr}_{0.49})_2\text{B}_2\text{P}_2\text{O}_{10}:0.02\text{Eu}^{2+}$ phosphor is (0.29, 0.25). The result shows that it is a potential bluish white emitting phosphor for white LEDs.

References

- [1] Guo Chongfeng, Yu Jie, Ding Xu, Li Ming, Ren Zhaoyu and Bai Jintao, *Journal of the Electrochemical Society* **158**, J42 (2011).
- [2] Song Yanhua, Jia Guang, Yang Mei, Huang Yeju, Hou Hongpeng and Zhang Hongjie, *Applied Physics Letters* **94**, 091902-1 (2009).
- [3] Zhou Jun, Wang Yuhua, Liu Bitao and Li Feng, *Journal of Applied Physics* **108**, 033106-1 (2010).
- [4] Ma Liang, Wang Da-Jian, Mao Zhi-Yong, Lu Qi-Fei and Yuan Zhi-Hao, *Applied Physics Letters* **93**, 144101-1 (2008).
- [5] Jiang Ziqiang and Wang Yuhua, *Electrochemical and Solid-State Letters* **13**, J68 (2010).
- [6] Li Panlai, Wang Zhijun, Yang Zhiping and Guo Qinglin, *Journal of Rare Earths* **28**, 523 (2010).
- [7] Zheng Xi, Fei Qinni, Mao Zhiyong, Liu Yanhua, Cai Yi, Lu Qifei, Tian Hua and Wang Dajian, *Journal of Rare Earths* **29**, 522 (2011).
- [8] Zhang Gongguo, Wang Jing, Chen Yan and Su Qiang, *Optics Letters* **35**, 2382 (2010).
- [9] Tang Yu-sheng, Hu Shu-fen, Ke Wei-chih, Lin Chun Che, Bagkar Nitin C. and Liu Ru-shi, *Applied Physics Letters* **93**, 131114-1 (2008).
- [10] Liang Chih-Hao, Chang Yee-Cheng and Chang Yee-Shin, *Applied Physics Letters* **93**, 211902-1 (2008).
- [11] Bandi Vengala Rao, Nien Yung-Tang and Chen In-Gann, *Journal of Applied Physics* **108**, 023111-1 (2010).
- [12] Wang Zhijun, Yang Zhiping, Guo Qinglin, Li Panlai and Fu Guangsheng, *Chinese Physics B* **18**, 2068 (2008).
- [13] Guo Chongfeng, Xu Yan, Ding Xu, Li Ming, Yu Jie, Ren Zhaoyu and Bai Jintao, *Journal of Alloys and Compounds* **509**, L38 (2011).
- [14] Park W. J., Song Y. H. and Yoon D. H., *Materials Science and Engineering B* **173**, 76 (2010).
- [15] Yuan Shuanglong, Chen Xianlin, Zhu Chaofeng, Yang Yunxia and Chen Guorong, *Optical Materials* **30**, 192 (2007).
- [16] Lan Yuwei, Yi Linghong, Zhou Liya, Tong Zhangfa, Gong Fuzhong and Wang Rongfang, *Physica B* **405**, 3489 (2010).
- [17] Zhang M., Wang J., Ding W., Zhang Q. and Su Q., *Applied Physics B* **86**, 647 (2007).
- [18] Kuo Te-Wen, Liu Wei-Ren and Chen Teng-Ming, *Optics Express* **18**, 1888 (2010).
- [19] Wang Peng, Song Jun, Tian Hua, Lu Qi-fei and Wang Da-jian, *Optoelectronics Letters* **8**, 201 (2012).
- [20] Liu Yan-hua, *Optoelectronics Letters* **6**, 34 (2010).
- [21] Davidenko N. K. and Yatsimirskii K. B., *Theoretical and Experimental Chemistry*, New York: Springer, 505 (1973).