

Luminescent properties of new bluish white $\text{CaBi}_2\text{B}_2\text{O}_7:\text{Dy}^{3+}$ phosphor for white light-emitting diodes

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A new Dy^{3+} -doped $\text{CaBi}_2\text{B}_2\text{O}_7$ bluish white phosphor has been prepared by solid-state reaction method. X-ray diffraction (XRD) and photoluminescence (PL) characterization have been carried out to verify the phase purity and the luminescence performance of prepared phosphors, respectively. This phosphor could be efficiently excited by 349 nm light features satisfactory bluish white emitting property. The optimum doping content of Dy^{3+} ions in the $\text{CaBi}_2\text{B}_2\text{O}_7$ host was found and the critical transfer distance was calculated. The results demonstrate that $\text{CaBi}_2\text{B}_2\text{O}_7:\text{Dy}^{3+}$ is a potential bluish white emitting candidate for near-UV pumped white LED.

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1. Introduction

In recent years, the solid-state lighting (SSL) for light emitting diode (LED) is considered to be the next-generation lighting source due to its low energy consumption, high efficiency, long life time and low maintenance [1-4]. The recent commercial white LED is devised through dichromatic route by pumping the blue InGaN LED chip with a yellow-emitting YAG: Ce^{3+} phosphor [5-7]. However, this route suffers from the demerits such as low color rendering ($R_a < 80$) and high color temperature (CCT > 4500 K); because of the lack of red spectral component in the visible region [8, 9]. To solve to issue, an alternative route to obtain high performance white light is by pumping the near ultraviolet (NUV) LED chip with trichromatic phosphors [10, 11]. Thus, the developments of new phosphors, which can be efficiently excited by NUV light, have drawn considerable attention from scientists [12-14].

Recently, trivalent dysprosium (Dy^{3+}) rare-earth ion as an important activator of white phosphors has drawn great attention for the applications in the NUV pumped white LED [15, 16]. Typically, Dy^{3+} ion has a $4f^9$ electron configuration, and exhibits two emissions (blue and yellow) emissions in the visible region attributed to ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ transitions of Dy^{3+} ion, respectively [17, 18]. Furthermore, the emission light with appropriate chromaticity coordinates of Dy^{3+} doped can be achieved through suitable adjustment of the blue/yellow intensity ratio in Dy^{3+} -doped phosphor since the yellow emission of Dy^{3+} ions is especially hypersensitive to the local environment, whereas the blue emission of Dy^{3+} ions is not [19-21]. Thus, Dy^{3+} -doped phosphors can hue the

emission light from bluish white, white to yellowish white in different host. In particular, borate based phosphors have attracted attention due to their advantages of a high luminous efficiency, low synthesis temperature, and high chemical stability in many luminescent host candidates [22-24]. In 2008 Tu et al. firstly reported that the structure of $\text{CaBi}_2\text{B}_2\text{O}_7$ was orthorhombic structure with a space group of Pna 21 ($a = 8.937 \text{ \AA}$, $b = 5.477 \text{ \AA}$, $c = 12.591 \text{ \AA}$ and $V = 616.33 \text{ \AA}^3$) [25]. In our previously work, Tm^{3+} doped $\text{CaBi}_2\text{B}_2\text{O}_7$ has been reported and $\text{CaBi}_2\text{B}_2\text{O}_7$ host can be found several advantages in this work, such as good chemical stability and low synthesis temperature [26]. However, until recently, there is no report about the luminescence properties of Dy^{3+} -doped $\text{CaBi}_2\text{B}_2\text{O}_7$.

In this paper, the $\text{CaBi}_2\text{B}_2\text{O}_7:\text{Dy}^{3+}$ phosphor has been successfully prepared by solid state reaction method. The phase structure and luminescence properties of $\text{CaBi}_2\text{B}_2\text{O}_7:\text{Dy}^{3+}$ were studied. were also studied. The optimum doping concentration of Dy^{3+} ions in the $\text{CaBi}_2\text{B}_2\text{O}_7$ host was founded and the critical transfer distance was also calculated. All the results indicate that $\text{CaBi}_2\text{B}_2\text{O}_7:\text{Dy}^{3+}$ is a potential bluish white emitting material.

2. Experimental

2.1. Materials and method

A series of $\text{CaBi}_{2-x}\text{B}_2\text{O}_7:\text{x}\text{Dy}^{3+}$ ($x = 0.03, 0.05, 0.07, 0.09$ and 0.11) samples were prepared by solid state reaction method. The starting materials CaCO_3 (analytical reagent grade), Bi_2O_3 (analytical reagent grade), H_3BO_3

(analytical reagent grade, the amount of H_3BO_3 was added in excess about 5 % to compensate its evaporation losses during the high temperature synthesis process.) and Dy_2O_3 (99.9% purity) were stoichiometric weighted and ground together in an agate mortar. Then the mixture was transferred to a ceramic crucible and preheated at 400 °C for 1 h, and further sintered in the muffle furnace at 800 °C for 3 h in the air atmosphere. After reaction, the samples were cooled down to room temperature naturally by turning off the furnace and then were reground into powder.

2.2. Characterization

The phase purities of samples were tested by X-ray diffraction (XRD) patterns using Rigaku Ultima IV Advanced X-ray diffractometer with a $\text{Cu K}\alpha$ (40.0 KV, 30.0 mA) radiation ($\lambda = 1.5418 \text{ \AA}$). The diffuse reflectance spectrum was measured by using a Shimadzu UV-2500PC spectrophotometer. Photoluminescence excitation (PLE) and emission (PL) spectra were measured by Hitachi F-4600 spectrofluorometer equipped with a 150 W Xenon lamp as an excitation source. All the measurements were performed at room temperature.

3. Results

3.1. XRD analysis

Fig. 1 presents the XRD patterns of the as-prepared $\text{CaBi}_{1.93}\text{B}_2\text{O}_7:0.07\text{Dy}^{3+}$ phosphors. One can see that all the diffraction peaks of sample can be well indexed to the standard data card ICSD#245016 (the inset of Fig. 1 shows the $\text{CaBi}_2\text{B}_2\text{O}_7$ structure orthorhombic with a space group of Pna 21), indicating that a pure crystalline compound was obtained. The results suggest that the introduction of Dy^{3+} ions have not led to obvious change of lattice parameter in the $\text{CaBi}_2\text{B}_2\text{O}_7$ host structure.

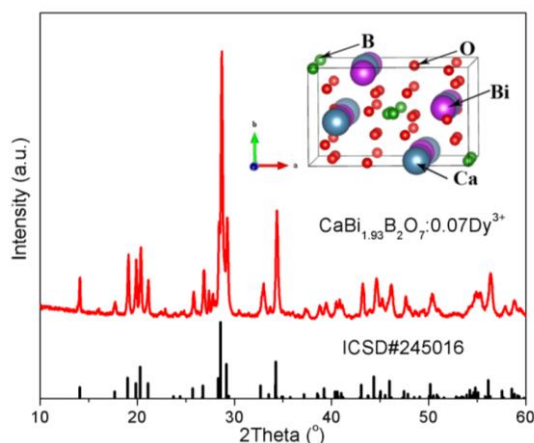


Fig. 1. XRD patterns of $\text{CaBi}_{1.93}\text{B}_2\text{O}_7:0.07\text{Dy}^{3+}$ phosphor. (The standard ICSD#245016 data card of $\text{CaBi}_2\text{B}_2\text{O}_7$ is provided as a reference.); Inset shows the detailed crystal structure of $\text{CaBi}_2\text{B}_2\text{O}_7$

3.2. Band gap analysis of $\text{CaBi}_2\text{B}_2\text{O}_7$ host

In order to further investigate the optical properties of the $\text{CaBi}_2\text{B}_2\text{O}_7$ host, the reflection of $\text{CaBi}_2\text{B}_2\text{O}_7$ host was measured. Fig. 2 shows the diffuse reflectance spectrum of $\text{CaBi}_2\text{B}_2\text{O}_7$ host. From Fig. 2, it is clearly observed that $\text{CaBi}_2\text{B}_2\text{O}_7$ has a band gap of approximately 3.41 eV. This result demonstrates that $\text{CaBi}_2\text{B}_2\text{O}_7$ host has a good UV transmission ability and is suitable for Dy^{3+} ions as a luminescent host.

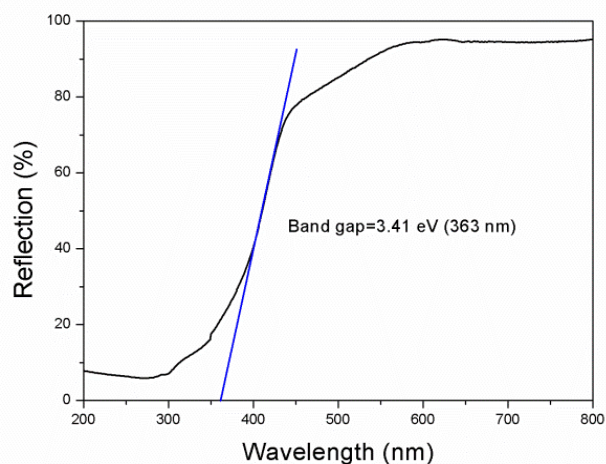


Fig. 2. Diffuse reflectance spectrum of the $\text{CaBi}_2\text{B}_2\text{O}_7$ host

3.3. Photoluminescence properties of $\text{CaBi}_2\text{B}_2\text{O}_7 \text{Dy}^{3+}$

The PLE spectrum ($\lambda_{\text{em}} = 462 \text{ nm}$) of $\text{CaBi}_{1.93}\text{B}_2\text{O}_7:0.07\text{Dy}^{3+}$ phosphor is depicted in Fig. 3. As shown in Fig. 3(a), the PLE spectrum of $\text{CaBi}_{1.93}\text{B}_2\text{O}_7:0.07\text{Dy}^{3+}$ was monitored at 476 nm. It consists of a group of narrow bands from 310 to 430 nm with peaks located at 324, 349, 364, 389 and 426 nm corresponding to the transitions of ${}^6\text{H}_{15/2} \rightarrow {}^4\text{K}_{15/2}$, ${}^6\text{H}_{15/2} \rightarrow {}^4\text{M}_{15/2}$, ${}^6\text{H}_{15/2} \rightarrow {}^4\text{P}_{3/2}$, ${}^6\text{H}_{15/2} \rightarrow {}^4\text{M}_{21/2}$ and ${}^6\text{H}_{15/2} \rightarrow {}^4\text{G}_{11/2}$ respectively [15, 27, 28]. Fig. 3 (b) shows the PL spectra ($\lambda_{\text{ex}} = 349, 364 \text{ and } 389 \text{ nm}$) of $\text{CaBi}_{1.93}\text{B}_2\text{O}_7:0.07\text{Dy}^{3+}$ sample indicate that the sample can be well excited by wavelengths of NUV light and its emission spectra are dominated by the ${}^4\text{F}_{15/2} \rightarrow {}^6\text{H}_{15/2}$ blue emission at 476 nm and ${}^4\text{F}_{15/2} \rightarrow {}^6\text{H}_{13/2}$ yellow emission at 574 nm with almost the same blue/yellow intensity ratios. It can also be found that the highest intensity is obtained when the excitation wavelength is 349 nm.

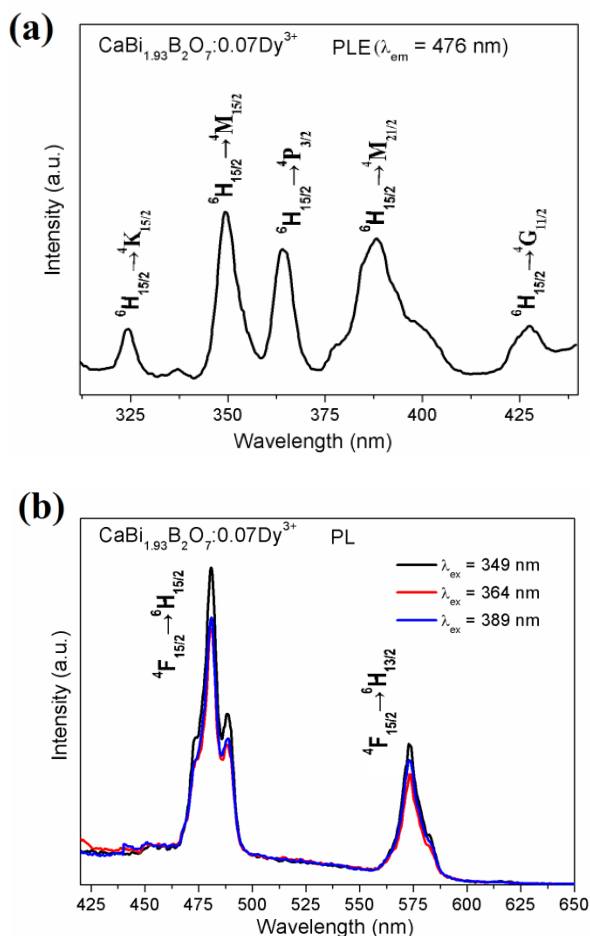


Fig. 3. (a): The PLE spectrum ($\lambda_{em}=476$ nm) of a typical $\text{CaBi}_{1.93}\text{B}_2\text{O}_7:0.07\text{Dy}^{3+}$ sample. (b): The PL spectra ($\lambda_{ex} = 349, 364$ and 389 nm) of a typical $\text{CaBi}_{1.93}\text{B}_2\text{O}_7:0.07\text{Dy}^{3+}$ sample

In order to further investigate the influence of content in the luminescence property of $\text{CaBi}_{2-x}\text{B}_2\text{O}_7:x\text{Dy}^{3+}$, the PL spectra of $\text{CaBi}_{2-x}\text{B}_2\text{O}_7:x\text{Dy}^{3+}$ ($x = 0.03, 0.05, 0.07, 0.09$ and 0.11) samples excited at 349 nm are shown in Fig. 4. One can see that all the PL spectra have no significant change is observed except their relative intensities. The relative intensities of $\text{CaBi}_{2-x}\text{B}_2\text{O}_7:x\text{Dy}^{3+}$ samples initially increases with the increase of Dy^{3+} content and then decreased after reaching the maximum at x is equal to 7.0 mol % due to the concentration quenching of Dy^{3+} ions. Blass has proposed that the concentration quenching of Dy^{3+} ions is highly dependent on the critical transfer distance R_c [29], which means the shortest average distance of the nearest activator Dy^{3+} ions at an optimal content. R_c can be obtained using the following equation:

$$R_c \approx 2 \left(\frac{3V}{4\pi x_c N} \right)^{1/3} \quad (1)$$

where V is the volume of the unit cell, x_c is the optimal content and N is the number of cations in the unit cell. For the $\text{CaBi}_2\text{B}_2\text{O}_7$ host, N is equal to 4 , x_c is equal to 0.07 and

V is equal to 616.33 \AA^3 , the value of R_c is calculated to be 16.14 \AA using Eq. (1).

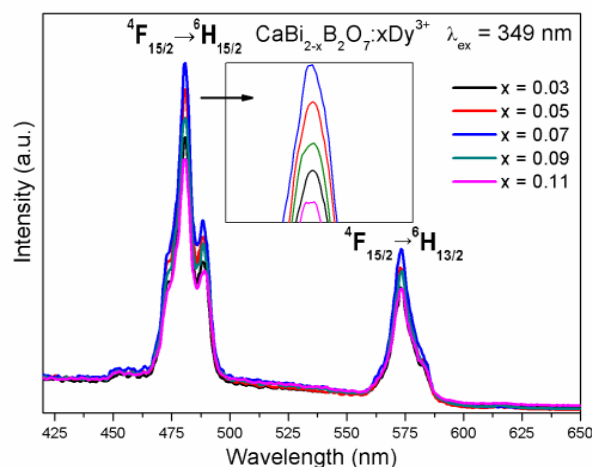


Fig. 4. The emission spectra of $\text{CaBi}_{2-x}\text{B}_2\text{O}_7:x\text{Dy}^{3+}$ ($x = 0.03, 0.05, 0.07, 0.09$ and 0.11) samples excited by 349 nm

3.4. CIE analysis

The PL spectrum of $\text{CaBi}_{1.93}\text{B}_2\text{O}_7:0.07\text{Dy}^{3+}$ sample was selected as an instance to study the CIE chromaticity coordinate performance of $\text{CaBi}_2\text{B}_2\text{O}_7:\text{Dy}^{3+}$ since all the samples show the similar emission shapes, and the sample $\text{CaBi}_{1.93}\text{B}_2\text{O}_7:0.07\text{Dy}^{3+}$ shows the strongest emission intensity among $\text{CaBi}_{2-x}\text{B}_2\text{O}_7:x\text{Dy}^{3+}$ samples. Based on the PL spectrum in the visible region under the 349 nm NUV light excitation, the CIE chromaticity coordinate has been calculated to be $(0.226, 0.228)$ by using the CIE 1931 color matching functions as reported [30] and the CIE chromaticity diagram of $\text{CaBi}_2\text{B}_2\text{O}_7:\text{Dy}^{3+}$ is shown in Fig. 5. It can be observed that the CIE chromaticity is located in the bluish white region, indicating that $\text{CaBi}_2\text{B}_2\text{O}_7:\text{Dy}^{3+}$ is a potential bluish white emitting material for the application in the near-UV pumped LEDs.

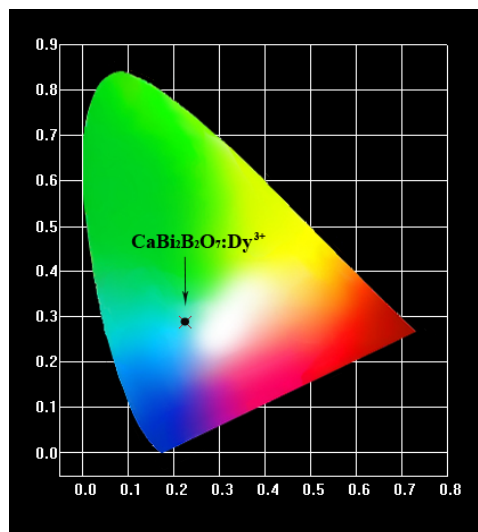


Fig. 5. CIE color coordinate diagram of $\text{CaBi}_2\text{B}_2\text{O}_7:\text{Dy}^{3+}$

4. Conclusion

In summary, a new Dy^{3+} -doped $\text{CaBi}_2\text{B}_2\text{O}_7$ bluish white phosphor has been prepared by conventional high temperature solid-state reaction method. This phosphor can be effectively excited by 349 nm NUV light and features bluish white emission due to the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ (blue) transitions and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ (yellow) transitions of Dy^{3+} ions, respectively. The optimum doping concentration of Dy^{3+} ions in the $\text{CaBi}_2\text{B}_2\text{O}_7$ host was founded to be around 7.0 mol% and the critical transfer distance was calculated to be 16.14 Å. The CIE color coordinate of $\text{CaBi}_2\text{B}_2\text{O}_7:\text{Dy}^{3+}$ under UNV light excitation is determined to be (0.226, 0.228), which is located in the bluish white region. All the results indicate that $\text{CaBi}_2\text{B}_2\text{O}_7:\text{Dy}^{3+}$ is a kind of potential bluish white emitting material for the application in the NUV pumped LED.

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References

- [1] G. Reddy, L. R. Moorthy, K. Pavani, B. Jamalalah, *Optoelectron. Adv. Mat.* **7**(9-10), 712 (2013).
- [2] G. Annadurai, S. M. M. Kennedy, *J. Lumin.* **169**, 690 (2016).
- [3] J. Chen, Y. Liu, L. Mei, H. Liu, M. Fang, Z. Huang, *Sci. Rep.* **5**, 9673 (2015).
- [4] K. Koparkar, N. Bajaj, S. Omanwar, *Optoelectron. Adv. Mat.* **9**(7-8), 915 (2015).
- [5] X. Huang, *Nat. Photonics* **8**, 748 (2014).
- [6] R. Yu, C. Guo, T. Li, Y. Xu, *Curr. Appl. Phys.* **13**(5), 880 (2013).
- [7] X. Wang, C. S. Liu, T. Yu, X. Yan, *Phys. Chem. Chem. Phys.* **16**(26), 13440 (2014).
- [8] H. D. Nguyen, C. C. Lin, M. H. Fang, R. S. Liu, *J. Mater. Chem. C* **2**(48), 10268 (2014).
- [9] J. Zheng, Q. Cheng, C. Zheng, G. Chen, F. Shi, C. Chen, *Funct. Mater. Lett.* **8**(6), 1550077 (2015).
- [10] J. Zheng, L. Ying, Q. Cheng, Z. Guo, L. Cai, Y. Lu, C. Chen, *Mater. Res. Bull.* **64**, 51 (2015).
- [11] J. Zhou, Z. Xia, M. Yang, K. Shen, *J. Mater. Chem.* **22**(41), 21935 (2012).
- [12] J. Liu, Z. Wu, M. Gong, *Appl. Phys. B* **93**(2), 583 (2008).
- [13] P. Pust, V. Weiler, C. Hecht, A. Tucks, A. S. Wochnik, A. K. Henss, D. Wiechert, C. Scheu, P. J. Schmidt, W. Schnick, *Nature Mater.* **13**, 891 (2014).
- [14] J. Hou, X. Yin, Y. Fang, F. Huang, W. Jiang, *Opt. Mater.* **34**(8), 1394 (2012).
- [15] H. Guo, F. Li, R. Wei, H. Zhang, C. Ma, J. Ballato, *J. Am. Ceram. Soc.* **95**(4), 1178 (2012).
- [16] X. Min, M. Fang, Z. Huang, Y. Liu, C. Tang, X. Wu, *Mater. Lett.* **125**, 140 (2014).
- [17] K. Pavani, J. S. Kumar, T. Sasikala, B. C. Jamalalah, H. J. Seo, L. R. Moorthy, *Mater. Chem. Phys.* **129**(1-2), 292 (2011).
- [18] C. Zhi-Peng, W. Yu-Hua, Z. Jia-Chi, *Chin. Phys. B* **19**(5), 057803 (2010).
- [19] J. Zheng, Q. Cheng, J. Wu, X. Cui, R. Chen, W. Chen, C. Chen, *Mater. Res. Bull.* **73**, 38 (2016).
- [20] R. Singh, S. Dhoble, *Bull. Mater. Sci.* **34**(3), 557 (2011).
- [21] M. Shang, C. Li, J. Lin, *Chem. Soc. Rev.* **43**(5), 1372 (2014).
- [22] G. M. Cai, H. X. Liu, J. Zhang, Y. Tao, Z. P. Jin, *J. Alloys Compd.* **650**, 494 (2015).
- [23] Z. Zhang, Y. Peng, X. Shen, J. Zhang, S. Song, Q. Lian, *J. Mater. Sci.* **49**(6), 2534 (2014).
- [24] Z. Liang, F. Mo, X. Zhang, L. Zhou, *J. Lumin.* **151**, 47 (2014).
- [25] Y. F. Kargin, S. Ivicheva, L. Shvorneva, M. Komova, V. Krut'Ko, *Russ. J. Inorg. Chem.* **53**(9), 1512 (2008).
- [26] G. Li, H. Yan, F. Yan, *Mate. Sci. Engineer. B* **209**, 56 (2016).
- [27] J. Wang, J. Wang, P. Duan, *J. Lumin.* **145**, 1 (2014).
- [28] P. You, G. Yin, X. Chen, B. Yue, Z. Huang, X. Liao, Y. Yao, *Opt. Mater.* **33**(11), 1808 (2011).
- [29] G. Blasse, *Phys. Lett. A* **28**(6), 444 (1968).
- [30] E. F. Schubert, *Light-Emitting Diodes*, 2nd ed. (Cambridge University Press, 2006 (chapter 17) p. 292).

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