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Synthesis and Luminescence Property of A Novel Blue-emitting BaKBP₂O₈:Eu²⁺ Phosphor

HUANG Jun¹, SHAO Zhi-meng¹, REN Yin-bao¹, ZHAO Qing-er¹,
HONG Jia-dan¹, WANG Qian¹, DENG De-gang^{1*}, YU Hua², XU Shi-qing^{1*}

(1. College of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, China;

2. College of Materials and Environmental Engineering, Hangzhou Dianzi University, Hangzhou 310018, China)

* Corresponding Authors, E-mail: dengdegang@cjlu.edu.cn; sxucjlu@hotmail.com

Abstract: Novel efficient blue phosphors Ba_{1-x}KBP₂O₈:xEu²⁺ were successfully synthesized by high-temperature solid state reaction. The structure and luminescence properties were characterized systematically by XRD and fluorescence spectra, respectively. The results show that Eu²⁺ doping does not produce significant changes for the crystal structure which remains pure tetragonal. Excitation spectrum (monitoring wavelength is 443 nm) is composed of the acromion at 307 nm due to host absorption, and the main peak at 346 nm due to 4f⁷-4f⁶5d transition Eu²⁺ ions. Under violet light excitation, the samples emit blue light. When the mole fraction of Eu²⁺ is 0.03, the emission spectrum has a maximum intensity. However, with further increase of the concentration of Eu²⁺, the emission spectrum intensity decreases, as a result of concentration quenching. At temperatures over 370 K, the intensity of the phosphors is still more than 50%. The CIE chromaticity coordinate of BaKBP₂O₈:Eu²⁺ is (0.176 6, 0.168 1).

Key words: phosphors; BaKBP₂O₈:Eu²⁺; blue-emitting

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一种新型蓝光 BaKBP₂O₈:Eu²⁺ 荧光粉的合成与性能研究

黄 君¹, 邵智猛¹, 任印宝¹, 赵情儿¹, 洪佳丹¹,
王 倩¹, 邓德刚^{1*}, 余 华², 徐时清^{1*}

(1. 中国计量学院 材料科学与工程学院, 浙江 杭州 310018; 2. 浙江电子科技大学 材料与工程工程学院, 浙江 杭州 310018)

摘要: 通过高温固相法成功合成了一种新型蓝光荧光粉 BaKBP₂O₈:Eu²⁺, 分别用 XRD 和荧光光谱表征了其结构与光学性能。结果表明, Eu²⁺ 的引入并没有显著改变其四方相的晶体结构。样品的激发光谱(监测波长为 443 nm)是由主晶格吸收的 307 nm 吸收肩与 Eu²⁺ 离子 4f⁷-4f⁶5d 跃迁的 346 nm 主峰组成。在紫光激发下, 样品的发射光谱为蓝色。当 Eu²⁺ 离子摩尔分数为 0.03 时, 样品的发射强度达到最大值。然而, 随着 Eu²⁺ 浓度的进一步增加, 由于浓度猝灭机制, 其发射强度开始降低。在超过 370 K 的温度下, 荧光粉样品的相对发光强度仍然超过 50%。BaKBP₂O₈:Eu²⁺ 的色坐标为(0.176 6, 0.168 1)。

关键词: 荧光粉; BaKBP₂O₈:Eu²⁺; 蓝光发射

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1 Introduction

Since 1997, Nichia chemical company successfully developed a blue light-emitting diode (LED), the semiconductor solid-state lighting technology has been rapid development. Because of their high efficiency, compactness, good material stability, long operational lifetime, energy saving and environmental protection, white-emitting diodes (LED) are increasingly widely used in backlight, general lighting, *etc.* and will be fourth-generation lighting following the incandescent, fluorescent and HID lamps^[1-7]. Currently, the most common approach for manufacturing white LEDs is using yellow-emitting Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce³⁺) phosphors with a blue InGaN/GaN LED chip. However, the white light obtained in this way has bad color reproduction, and the luminous intensity and colors easily affected by environmental conditions^[8]. To solve these problems, people try to use the near-ultraviolet (UV) radiation (350–410 nm) to excite trichromatic phosphor for achieving the white light. Because of the human eye less sensitive to 350–410 nm wavelength, the type of white LED is only determined by the color of the phosphor^[9].

At present, the blue phosphor excited by near ultraviolet study focused on aluminosilicate^[10], silicates^[11-16] and nitrogen oxide matrix^[17-21]. However, these materials generally have a higher sintering temperature, and easy deliquescent. In this way, Boron phosphate substrate which has lower sintering temperature and higher quantum efficiency is a potential three-color fluorescent material^[19]. As early as 100 years ago, boron phosphate group phosphor was synthesized^[21], recent studies have focused on the application in the high-pressure mercury of these materials, as well as the impact of structural changes in the law luminescent properties^[21].

In the phosphor material system, it was found Eu²⁺ ions can substitute for Ba²⁺ ions into the matrix lattice because Ba²⁺ ions and Eu²⁺ ions with the same ion valence, and the ionic radius of Ba²⁺ ion being larger radius than Eu²⁺ ions^[22]. With violet excitation, BaKBP₂O₈ matrix doped Eu²⁺ emit visi-

ble light. Moreover, such materials have advantage of high luminous efficiency, long life, good stability and aging resistance, strong UV absorption, *etc.* To the best of our knowledge, the blue-emitting phosphate phosphors of BaKBP₂O₈:Eu²⁺ have not been reported in the literature.

In this paper, a series of BaKBP₂O₈:Eu²⁺ samples were synthesized by conventional high-temperature solid-phase method, which can be effectively excited by near 443 nm violet and blue fluorescence emitted. We studied BaKBP₂O₈:Eu²⁺ phosphor structure, emission spectra, excitation spectra, doping concentration of Eu²⁺ affect on the emission spectrum and the excitation spectrum, and its CIE color coordinates.

2 Experiments

Ba_{1-x}KBP₂O₈:xEu²⁺ phosphors were prepared by solid-state reaction method under reductive atmosphere. The raw materials were BaCO₃ (A. R., 99.9%), K₂CO₃ (A. R., 99.9%), H₃BO₃ (A. R., 99.9%), NH₄H₂PO₄ (A. R., 99.9%) and Eu₂O₃ (A. R., 99.99%). Stoichiometric amounts of starting materials were thoroughly mixed in an agate mortar by grinding and sintered at 1 000 °C in reductive atmosphere (5% H₂/95% N₂) for 3 h.

X-ray diffraction (XRD) pattern was collected by an X-ray diffractometer (Bruker Axs D2 PHASER diffractometer) with Cu Kα radiation ($\lambda = 0.154\ 06\ \text{nm}$) over the angular range $10^\circ \leq 2\theta \leq 80^\circ$, operating at 30 kV and 10 mA. The excitation and emission spectrum of phosphors were recorded by a PL3-211-P spectrometer (HORIBA JOBIN YVON, America) and a 450 W xenon lamp was used as the excitation source. All tests were performed at room temperature.

3 Results and Discussion

XRD patterns of Ba_{1-x}KBP₂O₈:xEu²⁺ phosphors and BaKBP₂O₈ ICSD standard pattern are shown in Fig. 1. A single phase of Ba₂Ca(PO₄)₂ without any impurities was obtained and all of the peaks were in good agreement with the JCPDS card [BaKBP₂O₈,

ICSD 249930], indicated that the doped Eu^{2+} ions have no obvious influence on the structure of the host of BaKBP_2O_8 , even at various Eu^{2+} doping concentrations. The crystal space group is $I-42d$ (122), with unit cell parameters $a = 0.7202(2)$ nm, $b/c = 0.5036$, $c/a = 1.9856$, cell volume $V = 0.74172(43)$ nm³, and no generate impurity phase. Compared with the BaKBP_2O_8 standard card, the peak positions of the diffraction patterns shift toward larger angle, which is due to the substitution of the larger Ba^{2+} ions by the smaller Eu^{2+} ions.

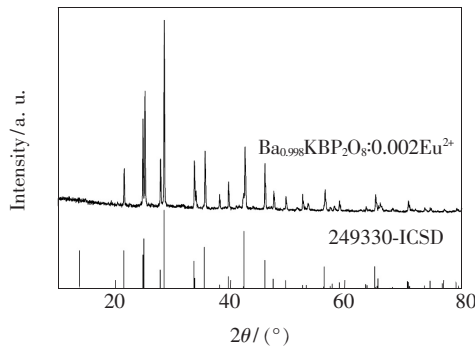


Fig. 1 XRD patterns of $\text{BaKBP}_2\text{O}_8 : \text{Eu}^{2+}$ phosphors and BaKBP_2O_8 ICSD standard pattern

Researchers carried out a detailed study on the crystal structure of BaKBP_2O_8 and the coordination of the central metal ion. The results showed that the crystal structure of BaKBP_2O_8 belongs to tetragonal which has $I-42d$ (122) space group, as shown in Fig. 2(a). P-O and B-O are both tetrahedron polyhedron, and K/Ba-O is eight coordination polyhedron, as shown in Fig. 2(b). The ionic radii of the eight-coordinated Ba^{2+} is 0.142 nm. Similarly, the ionic radii of the eight-coordinated Eu^{2+} is 0.139 nm, respectively. Because of the similarities of their ionic radii, Eu^{2+} ions are expected to randomly occupy Ba^{2+} ion sites in $\text{Ba}_{1-x}\text{KBP}_2\text{O}_8 : x\text{Eu}^{2+}$ crystal structure.

The excitation and emission spectra of $\text{Ba}_{0.98}\text{KBP}_2\text{O}_8 : 0.02\text{Eu}^{2+}$ phosphor are shown in Fig. 3. Excitation spectrum (monitoring wavelength 443 nm) is coverage for a wide spectrum of 270 – 410 nm with the full width at half maximum (FWHM) of 100 nm, which is composed of the absorption at 307 nm due to host absorption, and the main peak at 346 nm due

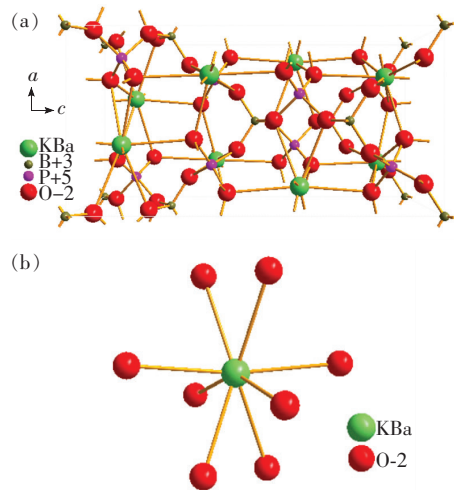


Fig. 2 (a) Crystal structure pattern of BaKBP_2O_8 . (b) Coordination pattern of K/Ba.

to $4f^7-4f^65d$ transition Eu^{2+} ions. Such phosphors can be used to violet chip at the emission peak of 365 nm. The emission spectra cover a wide range of wavelength 400 – 600 nm with the FWHM of 90 nm under 346 nm excitation. And its peaks at 443 nm, corresponding to Eu^{2+} ions $4f^65d-4f^7$ transition. In addition to the emission intensity changes, the emission peak of the emission spectra do not change significantly. It is proved that there is only one luminous environment in the matrix. Eu^{2+} ion luminescence covers all visible light emission from near UV to red. As the light-emitting is more easily affected by the environment in which the crystal field, the energy emitted wave is determined by its matrix environment. It is consistent with the above mention crystal structure analysis.

Excitation and emission spectra of $\text{Ba}_{1-x}\text{KBP}_2\text{O}_8 : x\text{Eu}^{2+}$ with different Eu^{2+} mole fraction are shown in

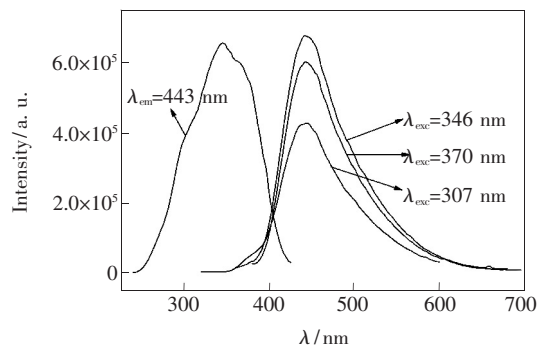


Fig. 3 Excitation and emission spectra of $\text{Ba}_{0.98}\text{KBP}_2\text{O}_8 : 0.02\text{Eu}^{2+}$

Fig. 4 and Fig. 5, respectively. As can be seen in Fig. 4, the peak shape of the excitation spectrum substantially unchanged with increasing the concentration of Eu²⁺ ions. As shown in Fig. 5, under 346 nm excitation, the position of emission peak happened red shift with the increase of Eu²⁺ concentration, and the intensity of the emission spectra changed significantly.

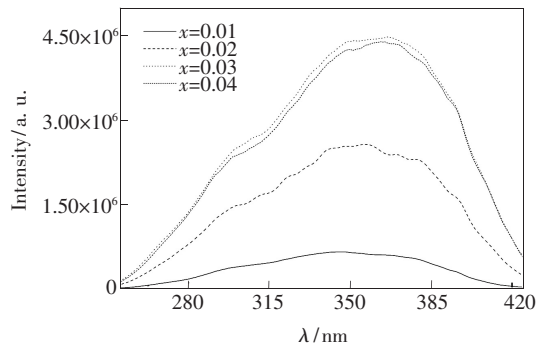


Fig. 4 Excitation spectra of Ba_{1-x}KBP₂O₈:xEu²⁺ with different Eu²⁺ mole fraction

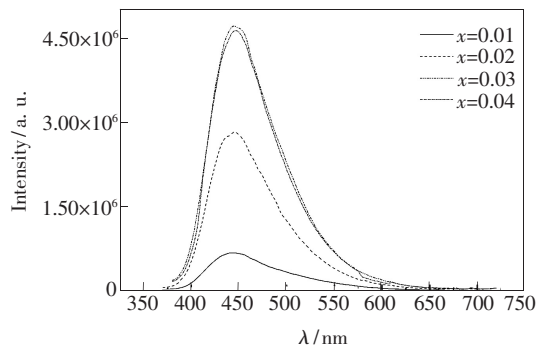


Fig. 5 Emission spectra of Ba_{1-x}KBP₂O₈:xEu²⁺ with different Eu²⁺ mole fraction

The emission intensity of Ba_{1-x}KBP₂O₈:xEu²⁺ with different Eu²⁺ mole fraction is shown in Fig. 6. The emission intensity increases with the increase of Eu²⁺ mole fraction up to a maximum x value of about 0.03, after which it decreases, as shown in Fig. 6. This is the result of concentration quenching. When the rate of energy transfer between Eu²⁺ ions increases rapidly greater than the transmission rate, the excitation energy can be consumed by lattice migration.

According to Dexter's theory^[23], we have calculated the critical distance between the Eu²⁺ ions for energy transfer by using the relation given by Blasse and Grabmaier^[24].

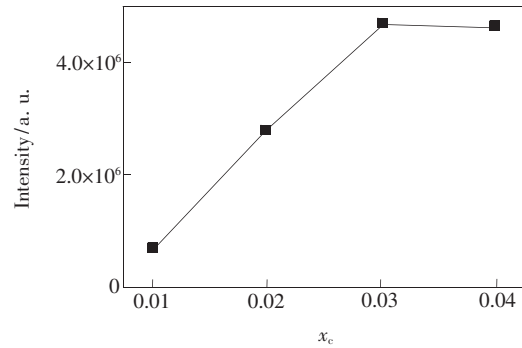


Fig. 6 Emission intensity of Ba_{1-x}KBP₂O₈:xEu²⁺ vs. Eu²⁺ mole fraction

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

where V is the volume of the unit cell, x_c is the critical concentration of activator, N is the number of formula units per unit cell. In BaKBP₂O₈ phosphor activated by Eu²⁺, $V = 0.74172 \text{ nm}^3$, $x_c = 0.03$, $N = 4$. The obtained R_c is 0.7076 nm.

Fig. 7 shows the temperature dependence of the relative emission intensity of Ba_{0.98}KBP₂O₈:0.02Eu²⁺ phosphor. We collect and processed the emission intensity of Ba_{0.98}KBP₂O₈:0.02Eu²⁺ phosphor monitored at 346 nm under a continuously change of operating temperature (K) to explore the effect on the thermal stability of the phosphor. With the increase of the temperature, while the thermal stability of the phosphor decreased gradually. In excess of 370 K, the intensity of the phosphors is still more than 50%.

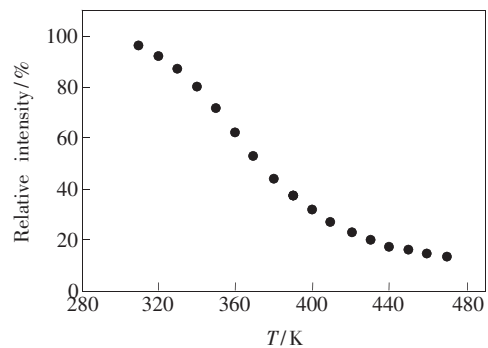


Fig. 7 Relationship of the emission intensity of Ba_{0.98}KBP₂O₈:0.02Eu²⁺ phosphor and operating temperature

The CIE chromaticity coordinates of Ba_{0.98}KBP₂O₈:0.02Eu²⁺ is shown in Fig. 8. The CIE chromaticity coordinates of BaKBP₂O₈:Eu²⁺ is (0.1766, 0.1681) in the blue region. The result reveals that BaKBP₂O₈:

Eu^{2+} is a potential blue-emitting phosphor for white LEDs.

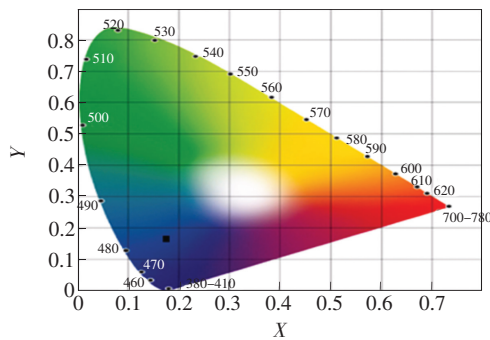


Fig. 8 CIE chromaticity coordinates of $\text{BaKBP}_2\text{O}_8:\text{Eu}^{2+}$

4 Conclusion

$\text{Ba}_{1-x}\text{KBP}_2\text{O}_8:x\text{Eu}^{2+}$ can be obtained by using conventional solid-state reaction method at 1 000 °C in a reductive atmosphere for 3 h and then cooled

down slowly to room temperature. Excitation spectrum of this phosphor is composed of the absorption at 307 nm due to host absorption, and the main peak at 346 nm due to $4f^7-4f^65d$ transition Eu^{2+} ions. Since there is only one light emitting environment in matrix, only one emission peak of the phosphor is located at 443 nm. The emission spectral intensity increases with the gradual increase of Eu^{2+} ions concentration, however, concentration quenching occurs finally. And the emission peaks red shift. The optimum distance of energy transfer between Eu^{2+} ions is 0.707 6 nm. At temperatures over 370 K, the intensity of the phosphors is still more than 50%. The CIE color coordinates indicate that the phosphors have higher efficiency in emitting blue light and better color purity than conventional phosphors at the near UV LED excitation.

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黄君(1990 -),男,浙江杭州人,硕士研究生,2013年于中国计量学院获得学士学位,主要从事稀土发光及荧光粉方面的研究。
E-mail: 410043564@qq.com



徐时清(1975 -),男,四川绵阳人,博士,教授,2005年于中国科学院上海光学精密机械研究所获得博士学位,主要从事光电功能材料与器件的研究。
E-mail: sxucjlu@hotmail.com