

Enhancing Luminescence of $\text{SrBPO}_5\text{:Sm}^{3+}$ Phosphor by Codoping Alkali Metal for White LEDs

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Abstract: An orange reddish phosphor $\text{SrBPO}_5\text{:Sm}^{3+}$ was synthesized by the traditional solid-state method. The phosphor component was characterized by the X-ray powder diffraction (XRD). The photoluminescence excitation (PLE) and emission spectra (PL) were investigated. The influence of the concentration of Sm^{3+} ions on luminescence properties of samples and concentration quenching mechanism were investigated. The results show that the as-prepared phosphor can be excited by 342 nm, 358 nm, 370 nm and 399 nm UV light and the strongest one at 399 nm. On being excited by 399 nm, the sample emits yellow, orange and red emission at different wavelength. The optimal activator molar fraction in this phosphor is 0.016 and the only sintering temperature is 1000°C. It is meant for enhancing the emission intensity of $\text{SrBPO}_5\text{:Sm}^{3+}$ phosphor if appropriate Li^+ ions are added as charge compensator. The thermal stability was evaluated by emission spectra of phosphor at different measuring temperatures. This research studied the influence of reaction temperature and charge compensator on the luminescence characteristics. The chromaticity coordinates of $\text{SrBPO}_5\text{:Sm}^{3+}$, R^+ phosphor was explored. The results indicate that $\text{SrBPO}_5\text{:Sm}^{3+}$, Li^+ is a potential orange-reddish phosphor in near UV based white LEDs.

Key words: luminescence; $\text{SrBPO}_5\text{:Sm}^{3+}$, Li^+ ; rare earth; spectral properties

Due to their intriguing characters such as durability, small volume, long lifetime and environment friendly, white light-emitting diodes (W-LEDs) are regarded as the next generation solid state lighting devices^[1-2]. The most common method for preparing the white light LEDs is by coating appropriate quantities of yellow emitting phosphor (YAG:Ce^{3+}) to a blue GaInN chip. However, the color rendering index of this kind of W-LED is low due to lack of the red light in the spectra^[3-4]. In order to improve the color rendering index, some red emitting phosphor can be added to the yellow phosphor. Otherwise, the W-LEDs combining with UV chip and tricolor phosphor attract more attention with the development of UV chip. Thus, the red phosphor that could be excited by UV light or blue is needed. Specifically, the Sm^{3+} doped phosphors exhibit a strong orange-red fluorescence and the excitation peak of these phosphors can match with UV chip very well^[5]. Some phosphor activated by Sm^{3+} ions are prepared and the luminescent properties are investigated. For example, $\text{Li}_2\text{BaP}_2\text{O}_7\text{:Sm}^{3+}$ ^[6], $\text{NaYP}_2\text{O}_7\text{:Sm}^{3+}$ ^[7], $\text{BaGd}_2\text{O}_4\text{:Sm}^{3+}$ ^[8],

$\text{Ca}_4\text{GdO(BO}_3)_3\text{:Sm}^{3+}$ ^[9], $\text{Ba}_3\text{La(PO}_4)_3$ ^[10], $\text{Y}_2\text{WO}_6\text{:Sm}^{3+}$ ^[11], $\text{Sr}_3\text{Sn}_2\text{O}_7\text{:Sm}^{3+}$ ^[12], $\text{Ba}_3\text{Bi(PO}_4)_3\text{:Sm}^{3+}$ ^[13], $\text{LiBaBO}_3\text{:Sm}^{3+}$ ^[14], $\text{Sr}_2\text{SiO}_4\text{:Sm}^{3+}$ ^[15], $\text{Y}_2\text{Si}_4\text{N}_6\text{C:Sm}^{3+}$ ^[16], etc.

The SrBPO_5 compound was first prepared by Bauer^[17]. SrBPO_5 belongs to indirect optical band gap materials and the gap between the conduction band minimum (CBM) and the valence band maximum (VBM) is about 5.663 eV. Thus, SrBPO_5 could be a category of good host for many luminescent ions due to the large band gaps.

In this study, we synthesized a reddish orange luminescent $\text{SrBPO}_5\text{:Sm}^{3+}$ phosphor and investigated its optical properties by measuring its photo-luminescent spectra with different Sm^{3+} concentration and charge compensator agent.

1 Experiment

$\text{SrBPO}_5\text{:Sm}^{3+}$, R^+ phosphors were synthesized by a solid-phase reaction method. The SrCO_3 (99.9%), H_3BO_3 (99.9%), $\text{NH}_4\text{H}_2\text{PO}_4$ (99.9%) and Eu_2O_3 (99.99%) were

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used as raw materials. The stoichiometrical raw materials were mixed thoroughly with alcohol in an agate mortar and were preheated at 400°C to get the precursor. Then, the precursor was sintered at 900°C for 4 h to get the products. Finally, the samples were grounded into powder for characterization. In this experiment, Li₂CO₃, Na₂CO₃ and K₂CO₃ are used as raw materials of charge compensator (Li⁺, Na⁺ and K⁺).

The crystal structures of the samples were collected on a Bruker D8 X-ray powder diffractometer with a CuK α radiation (40 kV, 40 mA). A Hitachi F-4600 spectro- photometer with Xe (150 W) lamp excitation source was used to record the fluorescence spectra. The whole measurements were operated at ambient temperature.

2 Results and discussions

2.1 Crystal structure of the SrBPO₅:xSm³⁺

The XRD patterns of SrBPO₅:xSm³⁺ phosphors are shown in Fig. 1(a). Obviously, all the diffraction peaks match well with the JCDPS card 54-0615, which demonstrates that no significant change to the crystal phases of the products caused by doping limited Sm³⁺ ions. The crystal lattice parameters are shown in Fig. 1(b) and both *a* and *c* are reduce with the concentration of Sm³⁺ ions iucrasing. It is generally recognized that Sm³⁺ ions will replace

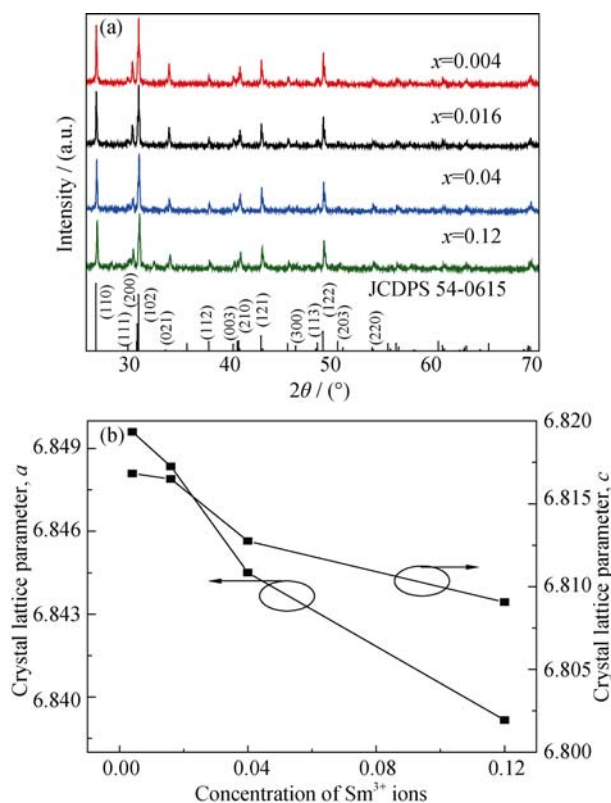


Fig. 1 XRD patterns of *x*Sm³⁺ doped SrBPO₅ phosphor (a) and influence of Sm³⁺ concentration on the crystal lattice parameters (b)

the sites of Sr²⁺ ions after entering the crystal lattice, while the ionic radius of Sm³⁺ ions (0.0964 nm) is smaller than that of Sr²⁺ ions (0.112 nm), which induces the lattice parameters decrease with the Sm³⁺ ions quantity.

2.2 Photoluminescence properties of SrBPO₅: Sm³⁺ phosphor

From Fig. 2, the photoluminescence excitation (PLE) spectra of Sr_{0.984}BPO₅ could be seen: 0.016Sm³⁺ monitoring for different emission peaks (598, 613, 561 and 644 nm). The excitation spectra take on similar shape though the intensity is different. It indicates that the excitation spectra composed of four narrow bands in the region of 300–420 nm and the excitation peaks locate at 342, 358, 370 and 399 nm, which is corresponding to the transition from ground level ⁶H_{5/2} to higher energy levels ³H_{7/2}, ⁴D_{5/2}, ⁶P_{7/2} and ⁴K_{11/2}, respectively. The strongest excitation peak lies at 399 nm, thus this phosphor can be excited by near UV light efficiently.

Photoluminescence (PL) spectra of Sr_{0.984}BPO₅: 0.016Sm³⁺ phosphor under 342, 358, 370 and 399 nm are illuminated in Fig. 3. The emission spectrum excited by 399 nm is strongest and all the emission spectra include three groups of emission bands. The main emission peaks

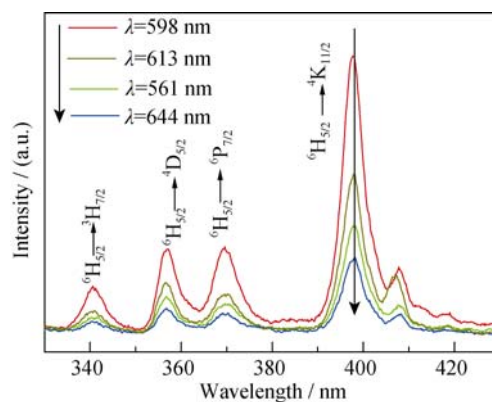


Fig. 2 Excitation spectra of SrBPO₅:Sm³⁺ phosphor monitoring for different emission peaks

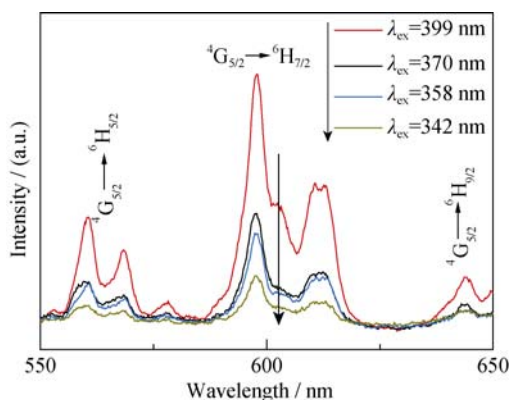


Fig. 3 Emission spectra of SrBPO₅:Sm³⁺ phosphor excited by different wavelength light

locate at 561 nm, 568 nm ($^4G_{5/2}$ to $^6H_{5/2}$), 598 nm, 610 nm ($^4G_{5/2}$ to $^6H_{7/2}$) and 613 nm ($^4G_{5/2}$ to $^6H_{9/2}$), which is assigned to the $f-f$ transitions of Sm^{3+} ions. Among the three groups of emission bands, the transition at 598 nm ($^4G_{5/2}$ to $^6H_{7/2}$) satisfies the selection rule of $\Delta J = \pm 1$ and it is a magnetic dipole (MD) and the other transitions belong to completely Electric dipole (ED) natured^[18].

It is obvious that the transition between Sm^{3+} ions and host is not observed and the interaction between them is very weak. The emission band from 590 nm to 620 nm is stronger than that of others; therefore this phosphor can emit orange-red light very well^[19].

Fig. 4 shows the possible energy transfer mechanism of Sm^{3+} ions. The Sm^{3+} ions transfer from ground state to excited state after absorbing energy and the energy state moves to the lowest excited energy level ($^4G_{5/2}$) through relaxation^[20].

2.3 Influence of Sm^{3+} ions on the luminescent properties of $SrBPO_5:Sm^{3+}$ phosphor

Fig. 5 shows that the intensity of emission peaks

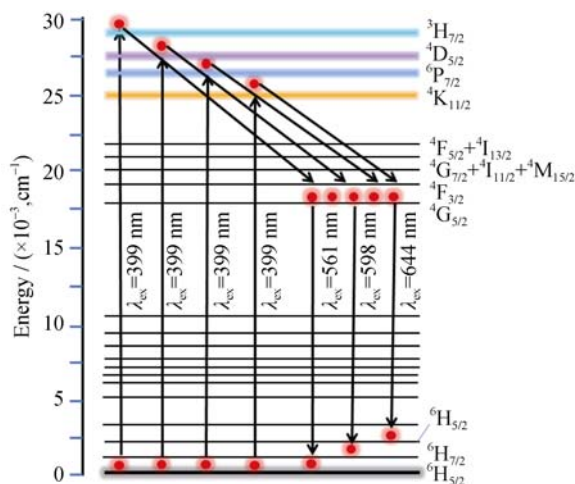


Fig. 4 Schematic energy level diagram of Sm^{3+} ions and the possible energy transfer

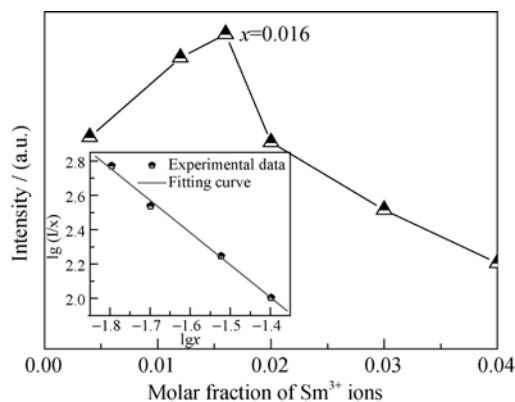


Fig. 5 Influence of Sm^{3+} concentration on the emission of $SrBPO_5:Sm^{3+}$ phosphor

increases with the concentration of Sm^{3+} ions from $x=0.002$ to $x=0.04$, thereafter, it decreases because of the concentration quenching. The concentration quenching ascribe to the distance between Sm^{3+} ions become shorter with the concentration and the energy transfer from one activator to another. The critical transfer distance (R_c) can be calculated by Blasse's equation^[21]:

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

Where V is the value of the unit cell of host, x_c is the Sm^{3+} ions concentration when the concentration quenching occur, N is the number of cations in the unit cell. For the $SrBPO_5$ host, $V=0.27687 \text{ nm}^3$, $N=3$, $x_c=0.016$, from Eq. (1) the value of R_c is about 2.23 nm.

Generally, the energy transfer will be induced by exchange interaction if the critical distance between the activator is shorter than 0.3~0.4 nm^[22]. Otherwise, it will be attributed to the multipolar interaction and the later is in point for $SrBPO_5:Sm^{3+}$ phosphor. On the basis of the theory of Dexter, the relationship between emission intensity (I) and activator concentration (x) could be expressed by this equation^[23]:

$$I \propto (1+A)/\gamma [\alpha^{1-s}/3\Gamma(1+s/3)] (\alpha \geq 1) \quad (2)$$

Where $\alpha = x(1+A)X_0/\gamma$, $\gamma^{3/s} \Gamma(1-s/3) \propto x$, x represents the activator concentration ($x=0.016$), s is the series of electric multipolar, γ represents the intrinsic transition probability of activator, A and X_0 are constant. The slope is the value of $s/3$ when a double logarithm coordinates is constructed using $\lg(I/x)$ and $\lg x$. When the value of s is 6, 8 and 10, the quenching mechanisms are dipole-dipole ($d-d$), dipole-quadrupole ($d-q$) and quadrupole-quadrupole ($q-q$), respectively. By calculating the slope of the curve from Fig. 4, the value of s is about 5.67(≈ 6), which manifests that $d-d$ interaction is the quenching mechanism of Sm^{3+} in $SrBPO_5:xSm^{3+}$ phosphor.

2.4 Influence of sintering temperature on the emission of $SrBPO_5:Sm^{3+}$ phosphor

The emission spectra of $SrBPO_5:Sm^{3+}$ phosphor sintered at different temperatures for 4 h are shown in Fig. 6. The emission intensity increase with the sintering temperature and the shape of spectra do not change which may be due to higher temperature that make the sample crystallize. Gradually, increasing the temperature will make sample sintering glass state. Thus 1000°C is the optimal sintering temperature for $SrBPO_5:Sm^{3+}$ phosphor.

2.5 Influence of charge compensator on the $SrBPO_5:Sm^{3+}$ phosphor

Sm^{3+} ions will replace the Sr^{2+} ions sites when they are introduced into the $SrBPO_5$ host due to the similar ions

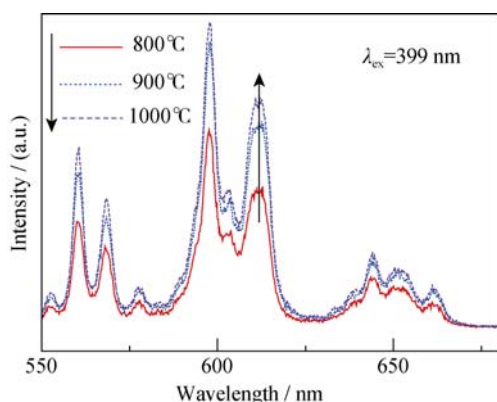
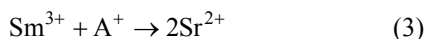


Fig. 6 Emission spectra of SrBPO₅:Sm³⁺ phosphor sintered at different temperatures

radii. This kind of displacement will introduce the charge imbalance for the non-equivalent substitution of Sm³⁺ for Sr²⁺ ions. An excess of positive charge in the lattice should be compensated to maintain the electro neutrality of SrBPO₅:Sm³⁺ phosphor. In our experiment, an alkali metal (A=Li⁺, Na⁺ or K⁺) is used to compensate the charge imbalance. The process can be expressed by Eq. (3) [24]:



As shown in Fig. 7, SrBPO₅ with 1.6mol% Sm³⁺ ion doping prepared from solid state reaction at 800°C exhibits red emission. The red emission intensity of the phosphors increased with the addition of equivalent molar Li₂CO₃ (Na₂CO₃ or K₂CO₃) charge compensation agent. Apparently, the optimal charge compensation agent is Li₂CO₃, which may be the Li⁺ ions with smaller radius and hence it is easy to enter the crystal lattice.

One of the significant factors for phosphor is color coordinates. In this case, the color coordinates for SrBPO₅:0.016Sm³⁺, 0.016Li⁺ is (0.58, 0.42), respectively, and they are given in the inset of Fig. 7. The value is computed using intensity calibrated emission spectra data and chromatic standard issues by the Commission International de l'Eclairage in 1931 (CIE 1931). The results indicate that this phosphor is a better orange phosphor.

2.6 Luminescence thermal stability of SrBPO₅: Sm³⁺, Li⁺ phosphor

Fig. 8 depicts the emission spectra under various temperatures excited by 399 nm (50°C to 250°C). The emission intensity has mild increase with the temperature and no temperature quenching occur, which indicates that the host material has better stability and is a kind of suitable material for phosphor.

3 Conclusions

In summary, a novel orange emitting phosphor SrBPO₅:

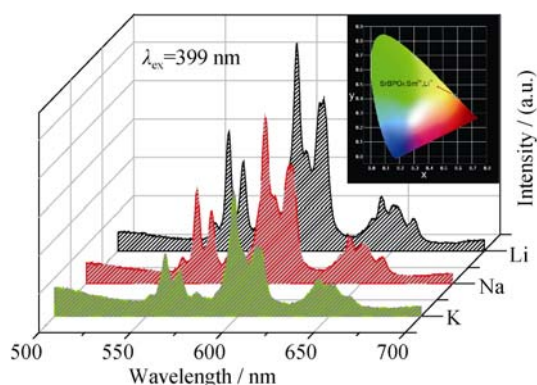


Fig. 7 Emission spectra of SrBPO₅:Sm³⁺ phosphor prepared with different charge compensators

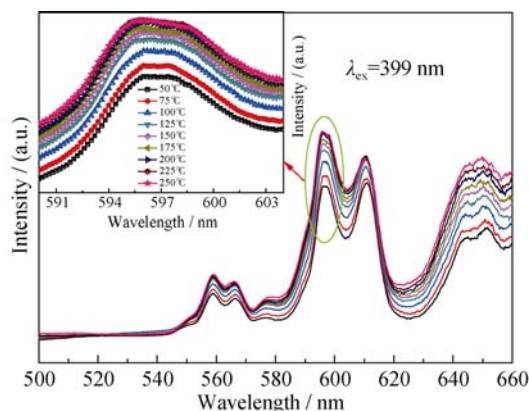


Fig. 8 Emission spectra of SrBPO₅:Sm³⁺, Li⁺ phosphor at different temperatures

Sm³⁺ was successfully prepared by solid phase reaction technology. This phosphor can be excited by 342 nm, 358 nm, 370 nm and 399 nm UV light and the strongest excitation peaks locates at 399 nm. There are three groups of emission peaks excited by 399 nm, which includes the yellow emission at 561 nm and 568 nm, the orange emission at 598 nm and 613 nm, and the red emission at 644 nm. The optimal activator molar fraction in this phosphor is 0.016 and the only sintering temperature is 1000°C. It is meant for enhancing the emission intensity of SrBPO₅:Sm³⁺ phosphor if appropriate Li⁺ ions are added as charge compensator. The results indicate that this phosphor is a better orange candidate for UV based white LED.

References:

- [1] KIM M, LEE S M, CHOI K C. Optical tuning of phosphors by plasmonic gold nanoparticles for phosphor-converted white light emitting diodes. *Appl. Phys. Lett.*, 2014, **105**: 141119–1–3.
- [2] YI S, CHUNG W J, HEO J. Stable and color-tailorable white light from blue LEDs using color converting phosphor glass composites. *J. Am. Ceram. Soc.*, 2014, **97**(2): 342–345.

- [3] JANG H S, IM W B, LEE D C, *et al.* Enhancement of red spectral emission intensity of $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ phosphor via Pr co-doping and Tb substitution for the application to white LEDs. *J. Lumin.*, 2007, **126**(2): 371–377.
- [4] CHIANG C H, LIU T H, LIN H Y, *et al.* Effects of flux additives on the characteristics of $\text{Y}_{2.95}\text{Al}_5\text{O}_{12}:0.05\text{Ce}^{3+}$ phosphor: particle growth mechanism and luminescence. *J. Appl. Phys.*, 2013, **114**: 243517.
- [5] ZHANG ZHI-WEI, SHEN XI-HAI, REN YAN-JUN, *et al.* Influence of Al^{3+} ions on the enhancement of the fluorescence in the $\text{CaMoO}_4:\text{Sm}^{3+}$ phosphor. *Opt. Laser. Tech.*, 2014, **56**: 348–353.
- [6] WANI J A, DHOBLE N S, KOKODE N S, *et al.* Synthesis and luminescence property of $\text{Li}_2\text{BaP}_2\text{O}_7:\text{Ln}^{3+}$ ($\text{Ln}=\text{Eu}, \text{Sm}$) phosphors. *J. Lumin.*, 2014, **147**: 223–228.
- [7] NOVAIS S M V, DOBROWOLSKA A, BOS A J J, *et al.* Optical characterization and the energy level scheme for $\text{NaYF}_4:\text{Ln}^{3+}$ ($\text{Ln}=\text{Ce}, \text{Sm}, \text{Eu}, \text{Tb}, \text{Yb}$). *J. Lumin.*, 2014, **148**: 353–358.
- [8] RAJU G S R, YU J. S. Novel orange and reddish-orange color emitting $\text{BaGd}_2\text{O}_4:\text{Sm}^{3+}$ nanophosphors by solvothermal reaction for LED and FED applications. *Spectrochimica Acta Part A: Molecular and Biomolecular spectroscopy*, 2014, **124**: 383–388.
- [9] RAO B V, RAMBABU U, BUDDHUDU S. Emission analysis of $\text{Sm}^{3+}:\text{Ca}_4\text{GdO}(\text{BO}_3)_3$ powder phosphor. *Mater. Lett.*, 2007, **61**: 2868–2871.
- [10] YU R J, NOH H M, MOON B K, *et al.* Photoluminescence characteristics of Sm^{3+} doped $\text{Ba}_3\text{La}(\text{PO}_4)_3$ as new orange-red emitting phosphors. *J. Lumin.*, 2014, **145**: 717–722.
- [11] MU ZHONG-FEI, HU YI-HUA, CHEN LI, *et al.* A single-phase, color-tunable, broadband-excited white light-emitting phosphor $\text{Y}_2\text{WO}_6:\text{Sm}^{3+}$. *Mater. Lett.*, 2014, **146**: 33–36.
- [12] LEI BING-FU, MAN SHI-QING, LIU YING-LIANG, *et al.* Luminescence properties of Sm^{3+} -doped $\text{Sr}_3\text{Sn}_2\text{O}_7$ phosphor. *Mater. Chem. Phys.*, 2010, **124**(2/3): 912–915.
- [13] YANG FU, YANG ZHI-PING, YU QUAN-MAO, *et al.* Sm^{3+} -doped $\text{Ba}_3\text{Bi}(\text{PO}_4)_3$ orange reddish emitting phosphor. *Spectrochimica Acta Part A: Molecular and Biomolecular spectroscopy*, 2013(**105**): 626–631.
- [14] LI PAN-LAI, WANG ZHI-JUN, YANG ZHI-PING, *et al.* Emission features of $\text{LiBaBO}_3:\text{Sm}^{3+}$ red phosphor for white LED. *Mater. Lett.*, 2009, **63**(9/10): 751–753.
- [15] HA M G, JEONG J S, HAN K R, *et al.* Characterizations and optical properties of Sm^{3+} -doped Sr_2SiO_4 phosphors. *Ceram. Int.*, 2012, **38**(7): 5521–5526.
- [16] SUN JIA-YUE, ZENG JUN-HUI, SUN YI-NING, *et al.* Synthesis and luminescence properties of novel $\text{Y}_2\text{Si}_4\text{N}_6\text{C}:\text{Sm}^{3+}$ carbonitride phosphor. *Cera. Inter.*, 2013, **39**(2): 1097–1102.
- [17] PENG MING-YING, DA N, KROLIKOWSKI S, *et al.* Luminescence from Bi^{2+} -activated alkali earth borophosphates for white LEDs. *Opt. Exp.*, 2009, **17**: 21169–21173.
- [18] MAY P S, METEALF D H, RICHARDSON F S, *et al.* Measurement and analysis of excited-state decay kinetics and chiroptical activity in the $^6\text{H}_7 \leftarrow ^4\text{G}_{5/2}$ transitions of Sm^{3+} in trigonal $\text{Na}_3[\text{Sm}(\text{C}_4\text{H}_4\text{O}_5)_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$. *J. Lumin.*, 1992, **51**(5): 249–268.
- [19] DENG S Q, XUE Z P, YANG Y H, *et al.* Template-free fabrication and luminescent characterization of highly uniform and monodisperse $\text{Y}_2\text{O}_3:\text{Sm}^{3+}$ hollow submicrospheres. *J. Mater. Sci. Tech.*, 2012, **28**: 666–672.
- [20] LEE G H, KIM T H, YOON C, *et al.* Effect of local environment and Sm^{3+} -codoping on the luminescence properties in the Eu^{3+} -doped potassium tungstate phosphor for white LEDs. *J. Lumin.*, 2008, **128**: 1922–1926.
- [21] GUAN LI, LIU CHONG, LI XU, *et al.* Synthesis and optical properties of $\text{KCaPO}_4:\text{Eu}^{2+}$ phosphor. *Mater. Res. Bull.*, 2011, **46**(9): 1496–1499.
- [22] GUO NING, HUANG YE-JU, YOU HONG-PENG, *et al.* $\text{Ca}_9\text{Lu}(\text{PO}_4)_7:\text{Eu}^{2+}, \text{Mn}^{2+}$: a potential single-phased white-light-emitting phosphor suitable for white-light-emitting diodes. *Inorg. Chem.*, 2010, **49**(23): 10907–10913.
- [23] DEXTER D L, JAMES H S. Theory of Concentration Quenching in Inorganic Phosphors. *J. Chem. Phys.*, 1954, **22**: 1063.
- [24] LI X, YANG Z P, GUAN L, *et al.* A new yellowish green luminescent material $\text{SrMoO}_4:\text{Tb}^{3+}$. *Mater. Lett.*, 2009, **63**: 1096–1098.

共掺碱金属对白光 LEDs 用 $\text{SrBPO}_5:\text{Sm}^{3+}$ 荧光粉发光的增强作用

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摘 要: 利用传统的高温固相法合成了一种橘红色 $\text{SrBPO}_5:\text{Sm}^{3+}$ 荧光粉。通过 X 射线衍射(XRD)确定荧光粉的组成, 研究了样品的光致激发(PLE)和光致发射(PL)光谱, 探究 Sm^{3+} 离子浓度对样品发光性能的影响及浓度猝灭机理, 通过测试不同温度下的发射光谱分析了样品的热稳定性, 研究反应温度和电荷补偿剂对发光性能的影响。最后讨论了 $\text{SrBPO}_5:\text{Sm}^{3+}$, R^{+} 荧光粉的色坐标。结果表明: $\text{SrBPO}_5:\text{Sm}^{3+}$, Li^{+} 是一种潜在的用于 UV 激发的白光 LED 的橘红色荧光粉。

关 键 词: 发光; $\text{SrBPO}_5:\text{Sm}^{3+}$; Li^{+} ; 稀土; 光谱性质

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