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Preparation and Package Performances of Red Phosphor for LED

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Abstract: $LiEuW_2O_8$ phosphor was prepared with lithium carbonate, europium oxide and tungsten oxide. The spectral properties and morphology were exhibited by fluorescence spectrometer and SEM, respectively. The result showed that there is a wide excitation spectrum of this phosphor being suitable for LED chips with near-ultraviolet(NUV), blue or green emission. Its emission peak locates at 615 nm, and the emission chromaticity coordinates are x = 0.666, y = 0.331; Milling obviously impacts on its morphology. Sulfide phosphor and $LiEuW_2O_8$ phosphor were encapsulated, respectively, to compare their properties, the result showed that the latter can also decrease color temperature, and more importantly, the luminous efficiency is less affected, it can keep 60 lm/W above when color temperature is 4 000 K.

Key words: $LiEuW_2O_8$; white LED; package; color temperature

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1 Introduction

With the advantages of long lifetime, saving energy consumption, environmental-friendly characteristics, light-emitting diode (LED) has been paid more and more attention in resent years. Especially, white LED (WLED) promoted by many countries and many large companies and develops very rapidly. At present, the most common and convenient method to obtain the white light is combining a yellow-emitting phosphor, for example, trivalent cerium activated yttrium aluminum garnet ($YAG:Ce^{3+}$) wavelength converter, with a GaN blue LED chip. However, there are some problems for such "Blue + Yellow: white LEDs", such as high color temperature, low color rendering index, but from the view of vision theory, the light with low color temperature is more favorable to the human eyes, furthermore high color rendering index can reduce visual illusion. To solve the two problems, the best method is that adding red phosphor in yellow's when packaging. There are two kinds of red phosphor suitable for low color temperature: sulfide and nitride. However, sulfide has insurmountable shortcomings: deliquescent, unstable; but for nitride it is high price though it has overcome the sulfide's shortcomings. Many manufactures engaged in package can't bear so high price. At present, it is urgent to develop a new red phosphor with high stability and low price suitable for low color temperature WLED.

The tungstate and molybdate red phosphor as new systems have gotten more and more attention in resent years[1~10]. They can be excited by NUV, blue light and green light while the excitation peaks are at 395 nm, 462 nm and 530 nm. The two phosphors can emit bright red light when excited by the above three wave band. In addition, tungstate and molybdate themselves have other advantages like:

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good stability, excellent thermal conductivity. From the above, we can conclude that they have broad prospects of research and application. The tungstate phosphor will be the research emphasis in this paper.

2 Experiments

2.1 Preparation of $LiEuW_2O_8$ by Solid State Method

The starting materials include 99.99% purity Eu_2O_3, 99.99% purity WO_3, ≥ 97% purity Li_2CO_3 and analytical reagent grade H_3BO_3 and alcohol. Fig. 1 is the flow scheme for the process of preparing $LiEuW_2O_8$. Firstly, weighing 19.07 g Li_2CO_3, 88 g Eu_2O_3, 116 g WO_3, 6.69 g H_3BO_3 and 600 mL alcohol accurately. Secondly, the materials were mixed together in a ceramic jar with 1 kg agate ball, then milling for 24 h. Thirdly, the mixture was taken out to dry, afterwards it was sieved 5 ~ 7 times (the more the better). At last, the mixture was put into high temperature furnace at 800 ~ 1 000 ℃ for 3 ~ 4 h.

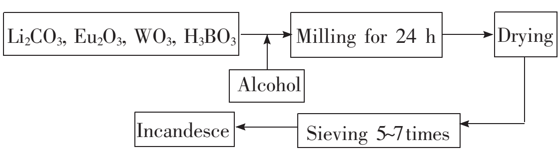

Fig. 1 The synthesis procedure of $LiEuW_2O_8$ by solid state method

2.2 Measurements

The structure of sample was examined by X-ray powder diffraction using Cu Kα radiation on a RIGAKU D max/RB X-ray diffractometer. The morphology and particle size of the phosphor were observed using JSM-5900 (JEOL, Japan) scan electron microscope. The spectra were measured at room temperature on a Donan 98 (Southeast University, China) luminescence spectrophotometer equipped with a xenon discharge lamp as an excitation source. The LED encapsulated with $LiEuW_2O_8$ was tested by ZWL3938 LED testing system (Hangzhou Zhongwei. Ltd., China).

3 Results and Discussion

The XRD patterns of $LiEuW_2O_8$ are shown in Fig. 2. The curve shows that $LiEuW_2O_8$ is of single phase and consistent with that given in JCPDS 25-0828 [$Na_{0.5}Gd_{0.5}MoO_4$]. It reveals that $LiEuW_2O_8$ has a scheelite structure with space group $I4_1/a$, the unit cell parameters are a = 0.520 8 nm, c = 1.128 2 nm. In this structure, Li^+ and Eu^{3+} occupy eight-coordinated sites; W^{6+} fills four-coordinated sites[6]. Due to the low temperature, the diffraction intensity of the sample prepared at 800 ℃ was weaker than that prepared at other three temperatures.

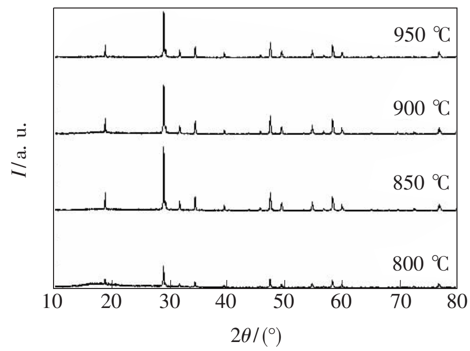

Fig. 2 XRD patterns of $LiEuW_2O_8$ phosphor prepared at different temperatures

Fig. 3 shows excitation and emission spectra of $LiEuW_2O_8$. The excitation spectrum [Fig. 3 (a)] roughly contains four absorption peaks. In the short wavelength range, there is a wide excitation band at 280 ~ 330 nm, which can be assigned to the charge transfer transitions of WO_4^{2-} and Eu—O. The curves in 360 ~ 530 nm range are intra-configurationally 4f-4f transitions of Eu^{3+} in the host lattices, and three of the stronger absorptions are at 395, 462 and 530 nm, which is attributable to the $^7F_0 \rightarrow {}^5L_6$ and $^7F_0 \rightarrow {}^5D_2$ transitions of Eu^{3+} for the former two, respectively. The excitation mechanism near 530 nm is still unclear. From the excitation spectra, it is known that $LiEuW_2O_8$ as a potential red phosphor for LED can match with various LED, such as NUV chip, blue- and green-lighting chip.

Fig. 3(b) is the emission spectra of $LiEuW_2O_8$ prepared at different temperatures. These lines show that the luminous intensity increases gradually with sintering temperature from 800 ℃ to 850 ℃, then decreases slowly from 850 ℃ to 950 ℃, and the intensity reaches a maximum value at 850 ℃. The sharp and position of the peak don't change with the sintering temperature changing. In the emission spectra of $LiEuW_2O_8$, the strongest emission peak is $^5D_0$-$^7F_2$ transition of Eu^{3+} at 615 nm, and other f-f transitions of Eu^{3+} are very weak, but they are advantageous to enhance the color-rendering index.

Of the phosphor and to obtain good CIE chromaticity coordinates. The CIE chromaticity coordinates for $LiEuW_2O_8$ are $x = 0.666\,5 \sim 0.668\,0$, $y = 0.330\,5 \sim 0.332\,0$, which is close to the NTSC (National Television Standard Committee) standard values.

Sulfide and nitride are two kinds of red phosphor for LED used past and now[11~13]. They both have wide excitation and emission spectra. The excitation spectrum of CaS: Eu locates in 450 ~ 550 nm, and emission spectrum locates in 620 ~ 690 nm, while excitation spectrum of nitride locates in 375 ~ 480, with its emission spectrum locates in 575 ~ 675 nm. From perspective of spectrum both of them are very suitable for low color temperature LED, but for their insurmountable shortcomings: deliquescent, unstable, high price. Sulfide has been disappearing gradually; the market of nitride is difficult to expand rapidly. Compared with them, $LiEuW_2O_8$ phosphor not only overcomes the disadvantages, but also posses their partial advantages. The only problem is that the use amount will be more than the above two when packaging.

Good morphology and proper particle size are considered to be a key technology to improve the phosphor brightness. Theory regards the phosphor particles in spherical or regular polyhedron are best to package. The luminous efficiency of LED will increase obviously if this phosphor was used in package because of their high bulk density, excellent lattice integrality. This is also the main reason of spray paralysis developing so rapidly in resent years. The sizes of particle have an important influence on package. In LED package, the big particles (>40 μm) are easy to precipitate, leading to poor optical-consistency; the crystal lattice of small particle (<5 μm) is destroyed seriously, leading to low luminous efficiency. Summarizing the above, we consider that the phosphors used in LED package should not be too large or too small; 15 ~ 30 μm may be the best size for high-power LED.

Fig. 4 is the SEM images of $LiEuW_2O_8$ phosphor prepared at 850 ℃. In the two images, the particle size is uneven, the sharp is irregular, and the small particles are sintered to be larger lumps (3 ~ 10 μm). Milling is the main reason leading to this result.

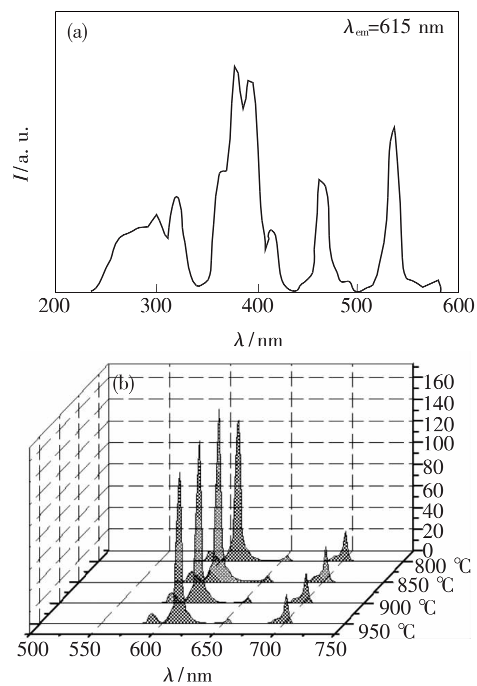

Fig. 3 Excitation spectrum (a) and emission spectrum (b) of $LiEuW_2O_8$ phosphor

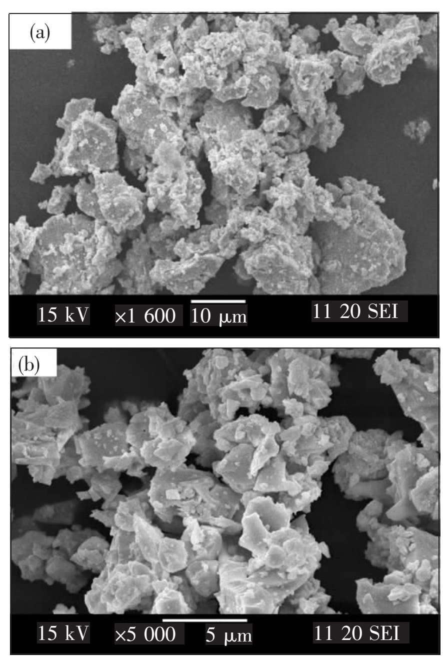

Fig. 4 SEM images of $LiEuW_2O_8$ phosphor prepared at 850 ℃, (a) 1 600 times; (b) 5 000 times.

It must to improve the grinding and classification method if we want to get suitable particle size.

In LED package, the different ratio between red phosphor and yellow phosphor leads to different luminous efficiency, color temperature, color-rendering index. In general case, the more amount of red phosphor, the lower luminous efficiency and color temperature, the higher color-rendering index, so each parameter should be considered comprehensive for package. In order to test the package performance of $LiEuW_2O_8$ phosphor, the mass ratio between silica and phosphor (red + yellow) is fixed as 0.5∶0.2; the mass ratio between red phosphor and yellow phosphor is adjustable. The specific proportions are shown in Table 1. For comparison, the package performance of sulfide is also studied under the same condition.

According to Table 1, taking the ratios to package and test, the results are shown in Table 2 and Table 3.

Table 1 The proportion of YAG and $LiEuW_2O_8$ (or CaS∶Eu) phosphor g

Number	YAG	$LiEuW_2O_8$
1	0.200	0
2	0.167	0.033
3	0.143	0.057
4	0.125	0.075
5	0.111	0.089
6	0.100	0.100
7	0	0.200

Table 2 The package results with different $LiEuW_2O_8$ ratios

Number	Luminous Efficiency/($lm \cdot W^{-1}$)	Color Coordinate(x,y)	Color temperature/K	Color-rendering index
1	77.8	0.307 0, 0.329 2	6 824	74
2	70.0	0.327 1, 0.358 0	5 722	73
3	68.0	0.353 2, 0.399 1	4 888	74
4	67.9	0.353 1, 0.401 4	4 892	74
5	67.8	0.377 0, 0.435 6	4 418	75
6	65.2	0.388 9, 0.457 6	4 256	76
7	10.5	0.151 0, 0.032 5	/	/

Table 3 The package results with different CaS∶Eu ratios

Number	Luminous Efficiency/($lm \cdot W^{-1}$)	Color Coordinate(x,y)	Color temperature/K	Color-rendering index
1	77.8	0.307 0, 0.329 2	6 824	74
2	44.41	0.376 1, 0.388 3	4 344	78
3	36.11	0.461 0, 0.460 0	3 043	80
4	34.25	0.412 9, 0.379 5	3 243	82
5	27.17	0.484 4, 0.398 8	2 424	85
6	25.8	0.478 6, 0.390 4	2 307	86
7	5.1	0.472 4, 0.186 7	1 001	/

As shown in Table 2, the luminous efficiency is declined gradually from 77.8 lm/W to 65.2 lm/W followed the color temperature declined from 6 824 K to 4 256 K while the amount of $LiEuW_2O_8$ increased from 0.02 g to 0.10 g. The color-rendering index has little change. The luminous efficiency of CaS∶Eu declined from 77.8 lm/W to 25.8 lm/W, and the color temperature declined from 6 824 K to 2 307 K followed the color-rendering index increased from 74 to 86 under the same condition as in Table 1. Comparing the seventh group in the two tables, the luminous efficiency of latter is only half of the former, when they are encapsulated individually. By comparing with each other, we can conclude that $LiEuW_2O_8$ has little influence on luminous efficiency, even it takes a half, this is a most important advantage, it can decrease the color temperature effectively; the sulfide has a serious influence on luminous efficiency, it is only one third of the initial value when the ratio reaches 50%, but on the other hand, it is effective to decrease the color temperature and increase the color-rendering index.

4 Conclusion

The red phosphor, $LiEuW_2O_8$ phosphor was prepared by solid state reaction. And its structure, luminescent property, morphology were investigated. The emission intensity reaches the highest at 850 ℃ with good color purity. The particles agglomerate obviously and the sizes are uneven and small. The package results shown that $LiEuW_2O_8$ phosphor had little influence on luminous efficiency and color-rendering index, certain influence on color temperature. Its stability is more higher than CaS∶Eu. Therefore, the $LiEuW_2O_8$ phosphor may be a good candidate for the red component of the white LED. In addition, To improve the fluorescence quantum yield is still the most important task at present.

References:

[1] Jing Yanjun, Wang Haibo, Huang Ruxi, *et al.* Red phosphor $LiEu(SiO_2)_{1/6}(WO_4)_2$ particles prepared by spray pyrolysis [J]. *Chin. J. Lumin.* (发光学报), 2007, **28**(5):715-719 (in Chinese).

[2] Yang Shuijin, Yu Xinwu, Sun Jutang, *et al.* Synthesis of Eu^{3+} doped Li_2WO_4 and its luminescence properties and ionic conductivity [J]. *Chemical Research and Application*, 2000, **12**(5):465-470.

[3] Yang Shuijin, Sun Jutang. Synthesis and luminescent properties of Eu^{3+} doped Li_2WO_4[J]. *Chin. Rare Earth* (稀土), 2004, **25**(1):17-19 (in Chinese).

[4] Lee Gwan Hyoung, Tae Hyung Kim, Chulsoo Yoon, *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]. *J. Lumin.*, 2008, **128**(12): 1922-1926.

[5] Wang Zhengliang, Liang Hongbin, Gong Menglian, *et al.* Novel red phosphor of Bi^{3+}, Sm^{3+} co-activated $NaEu(MoO_4)_2$ [J]. *Optical Materials*, 2007, **29**(7):896-900.

[6] Jiaguo Wang, Xiping Jing, Yan Chunhua, *et al.* Influence of fluoride on f-f transitions of Eu^{3+} in $LiEuM_2O_8$ (M = Mo, W) [J]. *J. Lumin.*, 2006, **121**(1):57-61.

[7] Zhang Guoyou, Zhao Xiaoxia, Meng Qingyu, *et al.* Preparation and properties of red emitting phospor $Gd_2Mo_2O_9$: Eu^{3+} for white LEDs [J]. *Chin. J. Lumin.* (发光学报), 2007, **28**(1):57-61 (in Chinese).

[8] 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**(7):93-96 (in Chinese).

[9] Gao Fei, Liang Lifang, Guo Chongfeng. Preparation and luminescence of red ligth-emitting phosphors based on $Li_3Ba_2Ln_{3-x}$-$(MoO_4)_8$ by sol-gel method [J]. *Chin. J. Lumin.* (发光学报), 2009, **30**(5):610-616 (in Chinese).

[10] Qi Faxin, Wang Haibo, Zhu Xianzhong. Spherical YAG: Ce^{3+} phosphor particles prepared by spray pyrolysis [J]. *J. Rare Earth*, 2005, **23**(4):892-895.

[11] Hu Yunsheng, Ye Hongqi, Zhuang Weidong, *et al.* Influence of Sr/Ca ratio on red phosphor $Ca_{1-x}Sr_xS$: Eu^{2+} [J]. *J. Chin. Rare Earth Soc.* (中国稀土学报), 2004, **22**(6):854-858 (in Chinese).

[12] Teng Xiaoming, Zhuang Weidong, Hu Yunsheng, *et al.* Luminescence properties of nitride red phosphor for LED [J]. *J. Rare Earth*, 2008, **26**(5):652-655.

[13] Oliver Oeckler, Florian Stadler, Tobias Rosenthal, *et al.* Real structure of $SrSi_2O_2N_2$[J]. *Solid State Sciences*, 2007, **9**(2):205-212.

LED红色发光粉的制备及封装性能

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摘要： 实验采用碳酸锂、氧化钨、氧化铕制备了 $LiEuW_2O_8$ 发光粉，通过扫描电镜和光谱仪分别研究了它的形貌与光谱特征。结果显示：$LiEuW_2O_8$ 发光粉的激发光谱较宽，非常适合于近紫外、蓝光及绿光芯片，发射光谱峰值位于615 nm，色坐标为（$x=0.666$，$y=0.331$）；球磨对它的形貌影响非常明显。为了比较硫化物发光粉和 $LiEuW_2O_8$ 发光粉的性能，分别对他们进行了封装实验，结果显示：$LiEuW_2O_8$ 发光粉能够有效降低色温，更重要的是，它对光效影响较小，4 000 K 时，光效可以保持在60 lm/W 以上。

关 键 词： $LiEuW_2O_8$；白光LED；封装；色温
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