Available online at www.sciencedirect.com

ScienceDirect

JOURNAL OF RARE EARTHS 25 (2007) 15 - 18

JOURNAL OF RARE EARTHS

www.elsevier.com/locate/jre

Photoluminescence Characteristics of $Gd_2Mo_3O_9$:Eu Phosphor Particles by Solid State Reaction Method

Zhao Xiaoxia (赵晓霞)[1,2], Wang Xiaojun (王晓君)[1*], Chen Baojiu (陈宝玖)[1,3], Meng Qingyu (孟庆裕)[1,2], Di Weihua (狄卫华)[1,2], Ren Guozhong (任国仲)[1,2], Yang Yanmin (杨艳民)[1,2]

(*1. Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China; 2. Graduate School of Chinese Academy of Sciences, Beijing 100039, China; 3. Department of Physics, Dalian Maritime University, Dalian 116026, China*)

Received 28 April 2006; revised 30 June 2006

Abstract: Eu^{3+}-doped $Gd_2Mo_3O_9$ was prepared by solid-state reaction method using Na_2CO_3 as flux and characterized by powder X-ray diffractometry. According to X-ray diffraction, this material belonged to a tetragonal system with space group $I4_1/a$. The effects of flux content and sintering temperature on the luminescent properties were investigated with the emission and excitation spectra. The results showed that flux content and sintering temperature had effects on the luminescent properties, the optimized flux content and the best temperature was 3% and 800 ℃, respectively. The excitation and emission spectra also showed that this phosphor could be effectively excited by C-T band (280 nm), ultraviolet light 395 nm and blue light 465 nm. The wavelengths at 395 and 465 nm were nicely fitting in with the widely applied output wavelengths of ultraviolet or blue LED chips. Integrated emission intensity of $Gd_2Mo_3O_9$:Eu was twice higher than that of Y_2O_2S:Eu^{3+} under 395 nm excitation. The Eu^{3+} doped $Gd_2Mo_3O_9$ phosphor may be a better candidate in solid-state lighting applications.

Key words: red emitting phosphor; Eu^{3+}; white LED; Na_2CO_3; rare earths

CLC number: TN949.16 **Document code**: A **Article ID**: 1002 - 0721(2007)01 - 0015 - 04

The research on the luminescent materials containing trivalent rare earth ions (RE^{3+}) has increased considerably in recent years[1,2]. Fluorescent materials have various applications in lighting and display industries. For example, Eu activated materials as red component have potential applications in color television displays[3,4].

Now-a-days light emitting diodes (LEDs) have emerged as an important class of source for white light. In 1997, the first white light emitting diodes became commercially available[5,6]. There are several ways to gain white light. One is the combination of a blue LED with a yellow phosphor, blending the blue light from the LED and yellow light from the phosphor results in white light. Its lighting efficiency is pretty good in the low current condition, but the color rendering is poor, because it only contains blue and yellow and other colors are excluded[3]. Another is the UV/violet light from LED exciting the tri-color phosphors to give white light. However, the phosphors that can be effectively excited by blue and NUV (near ultraviolet) light are deficient[7~10]. From then on, exploiting phosphors, which can be excited by blue light and near UV light emitted from LED, has become a

* **Corresponding author** (E-mail: zhaoxx97132@yahoo.com.cn)

Foundation item: Project supported by the National Natural Science Foundation of China (50572102, 50502031), Natural Science Foundation of Jilin Province (1999514, 20030514-2) and Outstanding Young People Foundation of Jilin Province (20040113)

Biography: Zhao Xiaoxia (1979 -), Female, Doctoral candidate

very active and interesting research subject. Host candidates, such as molybdates and tungstates, attract much attention because of some special properties of MoO_4^{2-} and WO_4^{2-} group. Neeraj S et al.[6] have reported the red phosphors $NaM(WO_4)_{2-x}(MoO_4)_x:Eu^{3+}$ (M = Gd, Y, Bi) and Wang Jiaguo et al.[11] have reported the red phosphors $Ca_{1-2x}Eu_xLi_xMoO_4$. Metal Mo can form different valence of Mo ions with the different preparation methods. In 1981, Jaganatha Gopalakrishnan et al.[12] reported hydrogen reduction of $Ln_2Mo_3O_{12}$ to $Ln_2Mo_3O_9$. To our best knowledge, there is no report on the spectroscopic properties of Eu^{3+} doped $Ln_2Mo_3O_9$.

In this letter, Eu^{3+} activated $Gd_2Mo_3O_9$ was prepared with solid-state reaction procedures in which Na_2CO_3 was introduced as a flux reagent. Various experimental factors affecting the luminescence property of $Gd_2Mo_3O_9:Eu$ were investigated.

1 Experimental

Phosphors were synthesized through the solid-state reaction technique. According to a certain stoichiometric ratio, the starting materials: gadolinium oxide (Gd_2O_3, 99.99%), europium oxide (Eu_2O_3, 99.99%) and molybdenum oxide (MoO_3, 99.99%) were weighted. $NaCO_3$ with purity of 99.9% was used as flux to improve the chemical reaction. After these powders were blended and grounded thoroughly in an agate mortar, the homogeneous mixture was obtained. The mixture was put into an alumina crucible and calcined in a muffle furnace at 600 ~ 1000 ℃ for 4 h, then the desirable samples were obtained.

The crystal structure of these phosphors was identified with a RigakuD/max-II B X-ray diffractometer (XRD) using Cu Kα (λ = 1.54178 nm) radiation at 40 kV and 100 mA. The excitation and fluorescence spectra of these powder phosphors were recorded on a Hitachi F-4500 using Xe lamp as excitation source. All the measurements were performed at room temperature.

2 Results and Discussion

2.1 Crystal structure

For the solid-state reaction, flux is often used to lower the sintering temperature, shorten the reaction time and improve the crystallization. Fig. 1 shows the XRD patterns of the sample prepared with different amount of Na_2CO_3. Obviously, the XRD pattern of the sample prepared with no flux is different from that of the samples prepared with Na_2CO_3 as flux reagent. Compared with the JCPDS card, it is known that sample with no flux is α-$Gd_2(MoO_4)$ (JCPDS card 25-0338) and the XRD patterns of the samples prepared with Na_2CO_3 agree well with $Gd_2Mo_3O_9$ structure (JCPDS card 33-0548). $Gd_2Mo_3O_9$ phosphor belongs to a tetragonal system with space group $I4_1/a$. The intensity of XRD peaks of sample with 3% Na_2CO_3 are higher than that of sample with 7% Na_2CO_3, indicating that 3% Na_2CO_3 as flux reagent is suitable.

2.2 Excitation and emission spectra

The excitation spectrum for monitoring $^5D_0 \rightarrow {}^7F_2$ emission of Eu^{3+} can be divided into two regions (as shown in Fig. 2): the broad excitation band extending up to 350 nm is attributable to the charge transfer transition of Eu – O and Mo – O group, and the narrow peaks located at wavelengths longer than 350 nm can be assigned to the f-f transitions of Eu^{3+}. The f-f transitions of Eu^{3+} in excitation spectrum include sharp lines $^7F_0 \rightarrow {}^5L_6(Eu^{3+})$ at 395 nm, $^7F_0 \rightarrow {}^5D_2(Eu^{3+})$ at 465 nm, and $^7F_0 \rightarrow {}^5D_1(Eu^{3+})$ at 535 nm; their intensities are comparable to the broad C – T band (in Fig. 3). For the usual Eu^{3+} doped phosphors the intensity of charge transfer band is much more stronger than that of f - f transitions in the excitation spectrum.

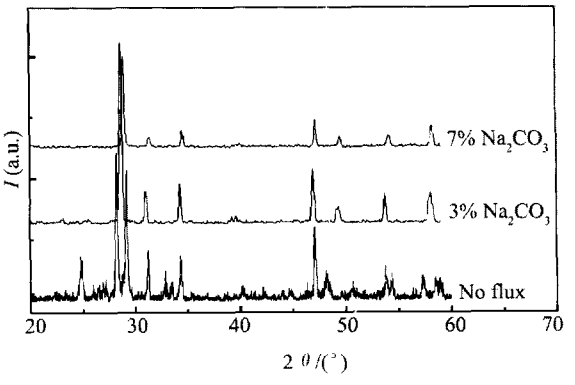

Fig. 1 XRD patterns of samples prepared at temperature of 800 ℃ with different amount of Na_2CO_3

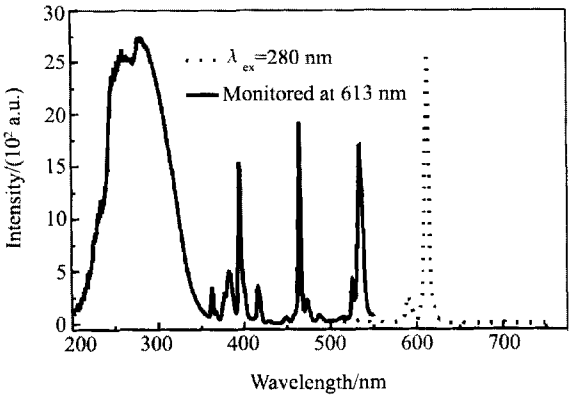

Fig. 2 Emission (dot line) and excitation (solid line) spectra for $Gd_{1.8}Mo_3O_9:Eu^{3+}_{0.2}$ phosphor

This abnormal phenomena was also observed in NaM $(WO_4)_{2-x}(MoO_4)_x$: Eu^{3+} (M = Gd, Y, Bi)[16] and AgLnMo_2O_8[13]. Probably, this is due to the nature of WO_4^{2-} and MoO_4^{2-} groups.

The emission spectrum of $Gd_{1.8}Mo_3O_9$: $Eu^{3+}_{0.20}$ excited upon 280 nm is shown in Fig. 2, composed of groups of several sharp lines, which belong to the intrinsic emission of trivalent Eu ion. The weak emission in the vicinity of 590 nm is ascribed to the Eu^{3+} magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$, which is insensitive to the site symmetry. The main emission line around 613 nm is assigned to the Eu^{3+} electric dipole transition of $^5D_0 \rightarrow {}^7F_2$, which is sensitive to the site symmetry. The domain emission peak at 613 nm indicates that the Eu^{3+} is located at the site lack of inversion symmetry breaking the parity selection rules. The emission spectra excited upon 395 and 465 nm (not shown here) have the same profile as that excited upon 280 nm. Obviously, this phosphor can be excited upon C - T band and f-f transition from the excitation spectra and emission spectra. It is a good sign that this novel phosphor can strongly absorb ultraviolet (395 nm) and visible blue light (465 nm), and transfer the excitation energy to the red radiation. The wavelengths at 395 and 465 nm are nicely in agreement with the widely applied UV or blue output wavelengths of GaN-based LED chips.

2.3 Effects of flux content and temperature on luminescence properties of sample

The effect of flux content on the integrated luminescent intensity of phosphor $Gd_{1.96}Mo_3O_9$: $Eu_{0.04}$ under NUV (395 nm) excitation illustrated in Fig. 3. With an increase of the flux dose, the integrated intensities of the phosphor are improved gradually until Na_2CO_3 amount to 3%. When the flux amount is more than 3%, the intensity of the phosphor decreases. This fact implies an identical conclusion from the XRD patterns (Fig. 1) that 3% flux could result in the best crystallization. So flux amount of 3% is a better choice to synthesis this phosphor.

Sintering temperature is an important factor affecting the luminescent properties of phosphors. Fig. 4 shows the emission spectra of the $Gd_{1.96}Mo_3O_9$: $Eu_{0.04}$ prepared at different temperatures excited upon 395 nm. The emission intensity of phosphor increases with an increase of preparation temperature below 800 ℃, and it is inverse above 800 ℃. It indicates that if the temperature is lower than 800 ℃, the reaction tends to form $Gd_2Mo_3O_9$, while the temperature is higher than 800 ℃, and other compounds different from $Gd_2Mo_3O_9$ crystal structure may grow. The intensity of PL emission in $Gd_{1.96}Mo_3O_9$: $Eu_{0.04}$ powders prepared at 800 ℃ was stronger than those of other temperatures, thus 800 ℃ is the optimized temperature to prepare $Gd_{1.96}Mo_3O_9$: $Eu_{0.04}$ phosphor.

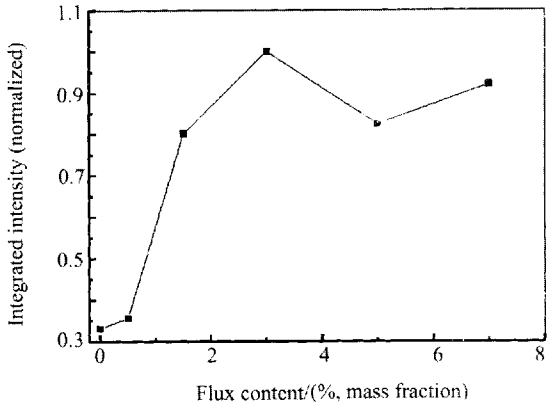

Fig. 3 Integrated emission intensity of $Gd_{1.96}Mo_3O_9$: $Eu_{0.04}$ plot as a function of flux reagent (Na_2CO_3) content under 395 nm excitation

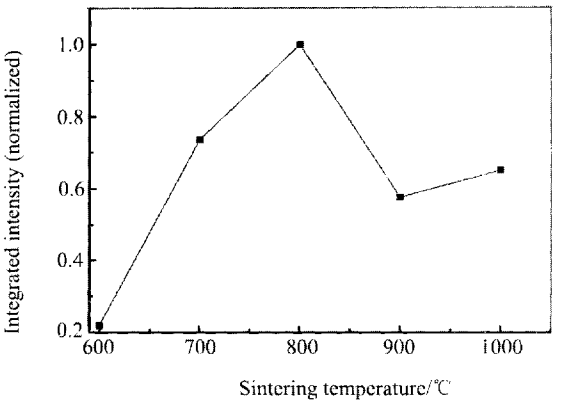

Fig. 4 Integrated emission intensities of $Gd_{1.96}Mo_3O_9$: $Eu_{0.04}$ prepared at different temperatures under 395 nm excitation

2.4 Comparison with Y_2O_2S:Eu red phosphor

Y_2O_2S: Eu is a well-known red photo-luminescent and cathodo-luminescent phosphor. It is widely appliee in cathode-ray tube due to its high luminous efficiency and better color satusation. At present, this phosphor was become a candidate red light materials for solid-state lighting application. The excitation spectra of Y_2O_2S: Eu and $Gd_2Mo_3O_9$: Eu are shown in Fig. 5 (left part). Obviously, the excitation spectrum in $Gd_2Mo_3O_9$: Eu shows a broad absorption band extending 350 nm and Y_2O_2S: Eu shows a broad band extending 390 nm. The excitation intensity of Y_2O_2S: Eu is much higher than $Gd_2Mo_3O_9$: Eu in the range from 200 to 380 nm, but the f-f transitions (395, 465

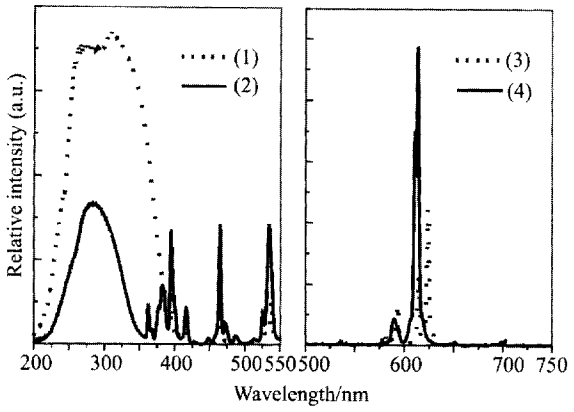

Fig. 5 Excitation spectra of $Y_2O_2S:Eu$ (curve (1)) and $Gd_2Mo_3O_9:Eu$ (curve (2)), and emission spectra under 395 nm UV excitation (curve (3) for $Y_2O_2S:Eu$ and curve (4) for $Gd_2Mo_3O_9:Eu$)

and 535 nm) of $Gd_2Mo_3O_9:Eu$ are stronger than those of $Y_2O_2S:Eu$.

Compared with the conventional phosphors $Y_2O_2S:Eu^{3+}$, as-synthesized phosphor exhibits a higher emission intensity when excited upon blue (465 nm) and UV (395 nm) light. The integrated intensity for $^5D_0 \rightarrow {}^7F_{1,2}$ transition of Eu^{3+} is twice higher than that of $Y_2O_2S:Eu^{3+}$ under 395 nm excitation (see right part of Fig. 5).

3 Conclusion

Eu^{3+}-doped $Gd_2Mo_3O_9$ was successfully developed through solid-state reaction with Na_2CO_3 as flux reagent. It was found that this phosphor could be effectively excited upon C – T band (280 nm) and ultraviolet light 395 nm and blue light 465 nm (f-f transition) and emited red light (613 nm) with line spectrum. The wavelengths at 395 and 465 nm were nicely fitting in with the widely applied output wavelengths of ultraviolet or blue LED chips. Appropriate amount of flux could enhance the luminescence intensity and improve crystallization. The result showed that the optimized flux content was 3%. The emission intensity of the sample prepared at 800 ℃ was stronger than those of other temperatures, indicating that 800 ℃ was the optimized temperature to prepare $Gd_2Mo_3O_9:Eu$ phosphor. Compared with the commercial phosphor $Y_2O_3S:Eu^{3+}$, the luminescent intensity of as-prepared phosphor $Gd_2Mo_3O_9:Eu$ was twice higher under 395 nm excitation. This novel phosphor may be a promising candidate for the white light emitting diodes in practical applications.

References:

[1] Kodaira C A, Brito H F, Malta O L, et al. Luminescence and energy transfer of europium (Ⅲ) tungstate obtained via the Pechini method [J]. *J. Lumin.*, 2003, **101**(1-2): 11.

[2] Lai Huasheng, Chen Baojiu, Wang Linsheng, Xu Wu, Wang Xiaojun, Xie Yihua, Ren Xinguang, Di Weihua. Characterization of (Y, Gd)$B_xV_{1-x}O_{4-x}$:Eu phosphor prepared by coprecipitation reaction [J]. *J. Rare Earths*, 2005, **23**(6): 668.

[3] Chou T W, Mylswamy S, Liu R S, et al. Eu substitution and particle size control of Y_2O_2S for the excitation by UV light emitting diodes [J]. *Solid State Commun.*, 2005, **136**(4): 205.

[4] Zhang Yue, Li Ya Dong. Red photoluminescence properties and crystal structure of sodium rare earth oxyborate [J]. *J. Alloys Compd.*, 2004, **370**(1-2): 99.

[5] Su Qiang, Wu Hao, Pan Yuexiao, Xu Jian, Guo Chongfeng, Zhang Xinmin, Zhang Jianhui, Wang Jing, Zhang Mei. Rare earth luminescent materials for white LED solid state lighting [J]. *Journal of the Chinese Rare Earth Society* (in Chin.), 2005, **23**(5): 513.

[6] Neeraj S, Kijima N, Cheetham A K. Novel red phosphors for solid-state lighting: the system $NaM(WO_4)_{2-x}(MoO_4)_x:Eu^{3+}$ (M = Gd, Y, Bi) [J]. *Chem. Phys. Lett.*, 2004, **387**(1-3): 2.

[7] Hu Yunsheng, Zhuang Weidong, Ye Hongqi, *et al*. A novel red phosphor for white light emitting diodes [J]. *J. Alloys Compd.*, 2005, **390**(1-2): 226.

[8] Park J K, Lim M A, Kim C H, et al. White light-emitting diodes of GaN-based $Sr_2SiO_4:Eu$ and the luminescent properties [J]. *Appl. Phys. Lett.*, 2004, **82**(5): 683.

[9] Park J S, Choi K J, Park S H, et al. Application of Ba^{2+}, Mg^{2+} co-doped $Sr_2SiO_4:Eu$ yellow phosphor for white light emitting diodes [J]. *J. Electrochem. Soc.*, 2005, **152**(8): H121.

[10] Kim J S, Park Y H, Choi J C, et al. Optical and structural properties of Eu^{2+}-doped $(Sr_{1-x}Ba_x)_2SiO_4$ phosphors [J]. *J. Electrochem. Soc.*, 2005, **152**(9): H135.

[11] Wang Jiaguo, Jing Xiping, Yan Chunhua, et al. $Ca_{1-2x}Eu_xLi_xMoO_4$: a novel red phosphor for solid-state lighting based on a GaN LED [J]. *J. Electrochem. Soc.*, 2005, **152**(3): G186.

[12] Jagannatha Gopalakrishnan, Arumugam Manthiram. Topochemically controlled hydrogen reduction of shceelite-related rare-earth metal molybdates [J]. *J. Chem. Soc. Dalton*, 1981, **3**: 668.

[13] Shi Fanian, Meng Jian, RenYufang. Structure and luminescent properties of three new silver lanthanide molybdates [J]. *J. Solid State. Chem.*, 1996, **121**(1): 236.