Synthesis and luminescent properties of novel red-emitting phosphor $InNbO_4:Eu^{3+}$ for white light emitting diodes

AN TANG[a,*], DINGFEI ZHANG[b], LIU YANG[c], HONGSONG ZHANG[a], HAOMING ZHANG[a], FENGXIANG SHAO[a], BO REN[a]

[a]*Department of Mechanical Engineering, Henan Institute of Engineering, Zhengzhou, Henan 451191, China*
[b]*College of Materials Science and Engineering, Chongqing University, Chongqing 400045, China*
[c]*Chongqing Academy of Science & Technology, Chongqing 401123, China*

Red-emitting phosphor $InNbO_4:Eu^{3+}$ was synthesized by solid-state reaction. The crystal structure, particle size distribution, and luminescence properties were respectively analyzed. The XRD pattern shows that pure $InNbO_4:Eu^{3+}$ was obtained. The spectra reveal that the phosphor can be effectively excited under excitation with 394 nm and 466 nm to emit strong red light at 612 nm due to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}. The perfect Eu^{3+}-doped concentration is 4 mol%. The chromaticity coordinates of the $InNbO_4:0.04Eu^{3+}$ are closer to the National Television Standard Committee (NTSC) standard values. Thus the $InNbO_4:Eu^{3+}$ is a promising red-emitting phosphor for white light emitting diodes.

(Received September 5, 2013; accepted January 22, 2014)

Keywords: Solid-state reaction, Phosphor, $InNbO_4$, Light emitting diodes

1. Introduction

Presently white light emitting diodes (LEDs) have been given much attention with the merits of long lifetime, low energy consumption, and environment friendliness [1,2]. Commonly a white LED can be achieved by combining a blue GaN-LED chip with a yellow phosphor [3]. However the color rendering index (CRI) and the luminous efficiency of this white light are low because of the deficiency of red component [4]. So many efforts have been devoted to the development of efficient red phosphors to compensate this shortcoming [5]. The current commercial red phosphors for white LEDs are sulfides such as $Y_2O_2S:Eu^{3+}$ [6]. But there exist some drawbacks to these sulfide-based phosphors including poor absorption, chemical unstability, and low luminescent intensities [7-9]. Hence, it is necessary to search for a novel red phosphor with high efficiency and good chemical stability. Niobates doped with rare earth ions can efficiently transfer energy to activators when they are excited by the excitation source [10,11]. Recently niobate as a red-emitting material for white LEDs has been paid great concern to by researchers. Huang et al. synthesized red phosphor $LaNbO_4:Eu^{3+}$, Bi^{3+} and resulted that it could emit brighter light at 615 nm with line spectra under the near UV light [12]. In this work, $InNbO_4:Eu^{3+}$ was prepared and its luminescent properties were investigated. The results aim at advancing the development of LEDs.

2. Experimental

Phosphor $InNbO_4:Eu^{3+}$ was synthesized by the high temperature solid-state method in air. In_2O_3 (99.99%), Nb_2O_5 (analytical grade), and Eu_2O_3 (99.99%) were used as starting powder materials. These individual materials were mixed and ground thoroughly in an agate mortar after they were stoichiometrically weighted out. The homogeneous mixture was preheated at 600℃ for 4h and calcined at 1255℃ for 6h. Then it was cooled with the furnace and the Phosphor $InNbO_4:Eu^{3+}$ was obtained. The structure of the phosphor was checked by X-ray diffraction (XRD) analysis with Cu Kα radiation at 40 kV and 150 mA. The particles size distribution was characterized by the Shimadzu SA-CP3. The excitation and emission spectra were measured by an RF-5301 molecular fluorescence spectrometer (excitation and emission slit width=3 nm). All the measurements were tested at room temperature.

3. Results and discussion

3.1 XRD analysis and size distribution characterization

The powder XRD pattern of $InNbO_4:0.04Eu^{3+}$ is shown in Fig. 1. The pattern agrees well with the given JCPDS No. 33-0619 and a single phase was obtained. A small amount Eu^{3+} ions doped in the phosphor have little influence on the host structure. According to the PDF card, $InNbO_4$ has a monoclinic crystal structure with a space group of *P2/a(13)* and its lattice parameter is *a*=0.5143 nm, *b*=0.5774 nm, *c*=0.4837 nm.

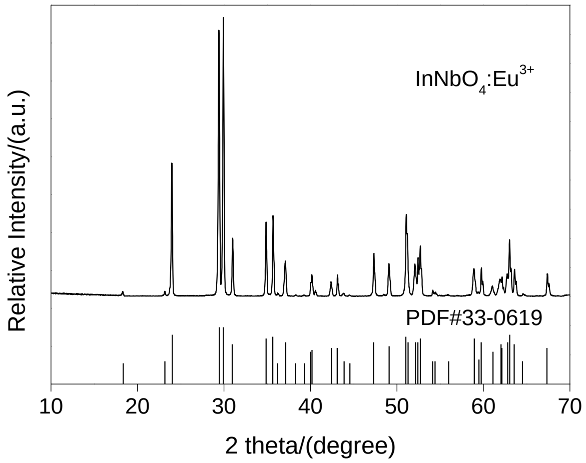

Fig. 1. XRD pattern of phosphor $InNbO_4:Eu^{3+}$.

Fig. 2 exhibits the particle size distribution of $InNbO_4:0.04Eu^{3+}$. The particles show a narrow size distribution with the average diameter of about 2.12 μm, which is fit for the fabrication of the solid-lighting devices [13].

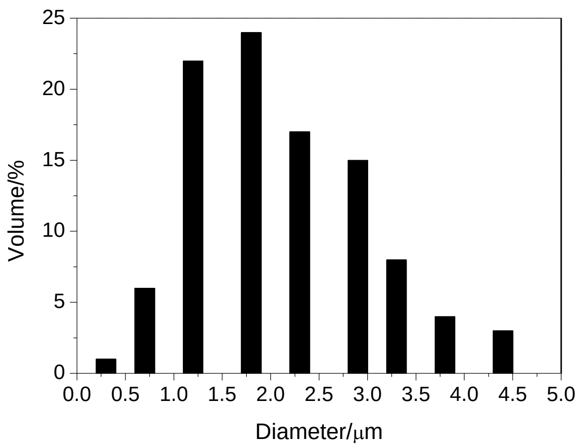

Fig. 2. Particle size distribution of $InNbO_4:Eu^{3+}$ phosphor.

3.2 Excitation and emission spectra of $InNbO_4:Eu^{3+}$ phosphor

Fig. 3 illustrates the excitation and emission spectra of the phosphor $InNbO_4:0.04Eu^{3+}$. The excitation spectrum consists of the broad band below 350 nm and some sharp bands beyond 350 nm. The former band is ascribed to the charge transfer (CT)[11,12]. The latter bands correspond to the intra-configurational 4*f*-4*f* transitions of Eu^{3+} in the $InNbO_4$. Two of stronger absorptions are respectively at 394 nm and 466 nm. It indicates that the phosphor can be effectively excited by the near-UV and blue wavelength lights. The emission spectrum has some peaks (i.e. 590, 612 nm) resulting from the characteristic $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 3 and 4) transition of Eu^{3+} [14]. Strong red emission at 612 nm was seen in the emission spectrum originating from the forced electric dipole transitions $^5D_0 \rightarrow {}^7F_2$. The emission spectrum is dominated by this red emission, which can concluded that the site occupied by Eu^{3+} in the host has a distorted cation environment [15]. This is helpful for the improvement of color purity for the red phosphor.

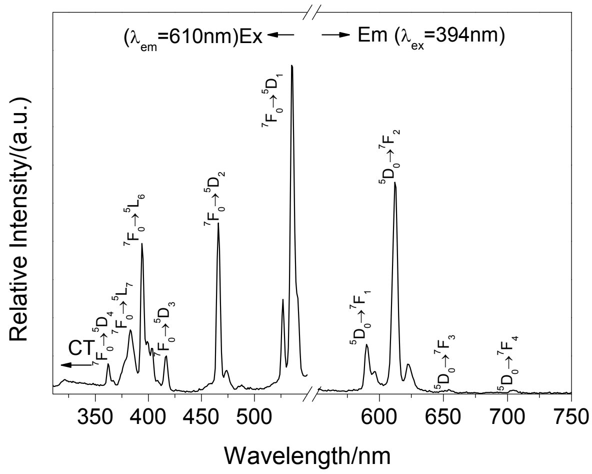

Fig. 3. The excitation (left) and emission (right) spectra of phosphor $InNbO_4:0.04Eu^{3+}$.

3.3 Effect of Eu^{3+} concentration on luminescence properties

The dependence of doping Eu^{3+} concentration in the phosphors on the relative intensity in the strongest $^5D_0 \rightarrow {}^7F_2$ transition is represented in Fig. 4. The $InNbO_4:Eu^{3+}$ phosphors exhibit the similar photoluminescence emission spectra except for the intensity. It can be observed that the intensity reaches a maximum value at 4 mol% and reduces with the increasing of the Eu^{3+} concentration beyond 4 mol%. This concentration quenching is generally owing to the lost of non-radiative transition. In this investigation, the optimal mole concentration of Eu^{3+} in the $InNbO_4:Eu^{3+}$ phosphor is 4 mol%.

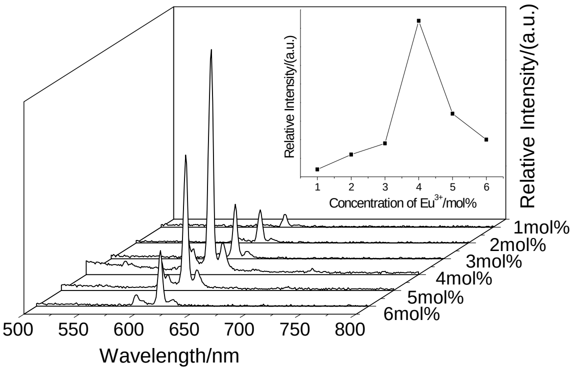

Fig. 4. Emission spectra (λ_{ex}=466 nm) of $InNbO_4$:Eu^{3+} phosphors with different Eu^{3+} concentration.

Table 1 lists the chromaticity coordinates of $InNbO_4$:Eu^{3+} phosphors. It can be found that the chromaticity coordinates (0.58, 0.33) of the phosphor $InNbO_4$:Eu^{3+} are closer to the National Television Standard Committee (NTSC) standard values (0.67, 0.33).

Table 1. The CIE chromaticity coordinates of the $InNbO_4$:Eu^{3+} (λ_{ex}=466 nm) with different content of Eu^{3+}.

Phosphor	CIE chromaticity coordinates☆	
	x	y
$InNbO_4$:0.01Eu^{3+}	0.58	0.31
$InNbO_4$:0.02Eu^{3+}	0.57	0.30
$InNbO_4$:0.03Eu^{3+}	0.58	0.32
$InNbO_4$:0.04Eu^{3+}	0.58	0.33
$InNbO_4$:0.05Eu^{3+}	0.57	0.33
$InNbO_4$:0.06Eu^{3+}	0.57	0.32

☆The NTSC standard values x=0.67, y=0.33.

4. Conclusions

In conclusion, the phosphor $InNbO_4$:Eu^{3+} was prepared by solid-state reaction. Upon excitation with 394 nm and 466 nm, the phosphor can emit strong red lines at 612 nm resulting from the forced electric dipole transitions $^5D_0 \rightarrow {}^7F_2$. The optimum Eu^{3+}-doped concentration in the phosphor $InNbO_4$:Eu^{3+} is 4 mol%. The CIE chromaticity coordinates (0.58, 0.33) of the $InNbO_4$:0.04Eu^{3+} are closer to the NTSC standard values. The results suggest that the Eu^{3+}-doped $InNbO_4$ is an attractive niobate red-emitting phosphor for white LEDs applications.

Acknowledgements

This work was supported by the Research Fund for the Doctoral Program of Henan Institute of Engineering (Grant No. D2013012), and Chongqing Sci&Tech Program (Grant No. CSTC2011GGB50012).

References

[1] P. L. Li, Z. J. Wang, Z. P. Yang, Q. L. Guo, X. Li, Mater. Lett. **63,** 751 (2009).
[2] Y. Q. Zhou, J. Liu, X. Y. Yang, X. B. Yu, J. Zhuang, J. Electrochem. Soc. **157,** H278 (2010).
[3] X. H. He, J. Zhou, N. Lian, J. H. Sun, M. Y. Guan, J. Lumin. **130,** 743 (2010).
[4] P. He, H. H. Wang, S. G. Liu, W. Hu, J. X. Shi, G. Wang, M. L. Gong, J. Electrochem.. Soc. **156,** E46 (2009).
[5] N. Xie, Y. L. Huang, X. B. Qiao, L. Shi, H. J. Seo, Mater. Lett. **64,** 1000(2010).
[6] C. F. Guo, W. Zhang, L. Luan, T. Chen, H. Cheng, D. X. Huang, Sensor. Actuat. B. **133,** 33 (2008).
[7] F. Xiao, Y. N. Xue, Q. Y. Zhang, Spectrochim. Acta A. **74,** 498 (2009).
[8] K. S. Hwang, S. Hwangbo, J. T. Kim, Ceram. Int. **35**, 2517 (2009).
[9] A. Tang, D. F. Zhang, L. Yang, X. H. Wang, Optoelectron. Adv. Mater. **5**, 1031 (2011).
[10] L. Pang, J. Lin, M. Yu, Solid state Chem. **177**, 2237 (2004).
[11] X. Z. Xiao, B. Yan, Mater. Lett. **61,** 1649 (2007).
[12] J. L. Huang, L. Y. Zhou, Z. P. Liang, F. Z. Gong, J. P. Han, R. F. Wang, J. Rare Earth. **28,** 356 (2010).
[13] R. P. Rao, J. Electrochem. Soc. **143,** 189 (1996).
[14] Z. H. Zhang, Q. Huang, X. Zhao, Z. L. Huang, Phys. Status Solidi A. **206,** 2839 (2009).
[15] L. Y. Zhou, J. S. Wei, J. R. Wu, F. Z. Gong, L. H. Yi, J. L. Huang, J. Alloy Compd. **476,** 390 (2009).

*Corresponding author: tangan527@126.com