

Journal of Alloys and Compounds 390 (2005) 220-222

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Crystal structure transformation and luminescent behavior of the red phosphor for plasma display panels

Zhijian Yu, Xiaowei Huang, Weidong Zhuang*, Xiangzhong Cui, Hongwei Li

National Engineering Research Center for Rare Earth Materials, General Research Institute for Non-ferrous Metals, and Grirem Advanced Materials Co. Ltd., Beijing 100088, China

Received 26 April 2004; accepted 8 July 2004

Abstract

To improve the chroma of red phosphor for plasma display panels, Eu^{3+} activated phosphors were prepared by combustion method, and were investigated in detail by XRD and PL spectra. With the decreasing of the amount of H₃BO₃, the phosphor crystal structures transform from hexagonal ortho-borate to monoclinic RE₃BO₆, and then to cubic oxide. The dominating emissions of the phosphors also change from ${}^{5}D_{0}-{}^{7}F_{1}$ transition to ${}^{5}D_{0}-{}^{7}F_{2}$ transition. Accordingly, CIE coordinates of the phosphors show that *x* values are increasing while *y* values are decreasing. Thus, phosphor with higher color purity could be achieved by adjusting the mole ratio of H₃BO₃. (© 2004 Elsevier B.V. All rights reserved.

Keywords: Phosphors; Chemical synthesis; Crystal structure and symmetry; Luminescence

1. Introduction

(Y,Gd,Eu)BO₃ is widely employed as red phosphor for plasma display panels (PDP) [1-3] for the high emission intensity under excitation of vacuum ultra violet (VUV) of 147 and 172 nm. However, the main emission line of the phosphor situates at 593 nm (in orange-red region), which leads to a low color purity [4]. Many works were carried out for years to improve the chroma properties. One of the ways is to introduce (Y,Eu)₂O₃ in coating process as red pigment. But the $(Y,Eu)_2O_3$ phosphor is known to have low light output under VUV excitation, which lead to a big loss of efficiency. Also vanadates and phosphates activated by Eu³⁺ had been tried to apply in PDP [5], which proved to be less efficient than the (Y,Gd)BO₃:Eu phosphor. Zhenggui Wei et al. reported that the emission intensity and color purity could be improved in nano-sized YBO3:Eu [6]. Considering lack of data on the forming process of this phosphor, phase transformation with the quantities of boric acid should be studied. In this work, phosphors activated by Eu³⁺ were prepared by combustion

* Corresponding author. *E-mail address:* wzhuang@chinarem.com (W. Zhuang).

0925-8388/\$ – see front matter M 2004 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2004.07.065

method. Results reveal that phosphor with certain amount of a new phase exhibits higher color purity than that of common ortho-borate phosphor while the relative brightness is almost equal.

2. Experimentals

According to our recent researches, nano-phosphor has higher quenching concentration than that of bulk ones [7]. In this work, we select mole ratio of Y, Gd, Eu as 0.45:0.4:0.15. The differences between compositions of the samples are that the content of H_3BO_3 is gradually decreased from 1.5 to 0 times of total RE quantities. The phosphors were prepared by combustion method using amino acetic acid as the combustion agent and then heated at 1000 °C for 30 min.

Luminescent spectra of the phosphors were measured by PDP-II Vacuum Ultraviolet spectro-radiometer (made in China). X-ray powder diffraction data were collected using a MXP21VAHF-M21X X-ray diffractometer having a CuKa radiation with the application of an electric current of 250 mA at an accelerating voltage of 40 kV.

3. Results and discussions

Crystal structure transformations of the phosphors could be interpreted by XRD patterns, which were illustrated in Fig. 1. According to the XRD patterns, when H₃BO₃ is 1.5, pure rare earth ortho-borate is produced. In this work, main structure type of the RE ortho-borate must be vaterite, as cations are heavier RE ions [8]: Y³⁺, Gd³⁺ and Eu³⁺. Difference between radii of the cations must lead to distortion in the vaterite structure. As the concentration of H_3BO_3 is decreased to 1.0–0.4, a new phase with monoclinic structure can be detected clearly. Compared with JCPDS No. 34-0291, the new phase may be RE₃BO₆. The monoclinic phase is very high in the sample with 1.0 mol H₃BO₃, which indicates that H₃BO₃ had not been fully used to build (Y,Gd,Eu)BO₃ crystal. That is, a small amount of H₃BO₃ was vaporized in the combustion process. The diffraction of RE₃BO₆ becomes weaker and weaker, when H₃BO₃ is gradually decreased. The phosphor with less than 0.4 mol H₃BO₃ exhibits pure cubic phase as common $(Y_{0.95}, Eu_{0.05})_2O_3$ phosphor, in which Eu^{3+} occupies C_2 and S_6 symmetry sites [9,10].

Reactions in the synthesis process might include the following processes. If there is no boric acid, Oxidation–reduction between combustion agent and RE nitrates will occur [11]:

$$6\text{RE}(\text{NO}_3)_3 + 10\text{H}_2\text{NCH}_2\text{COOH} + 18\text{O}_2 \rightarrow 3\text{RE}_2\text{O}_3 + 20\text{CO}_2 + 5\text{N}_2 + 25\text{H}_2\text{O} + 18\text{NO}_2$$
(1)

The reaction will finish in less than 1 min. When boric acid is added in the reaction, it decomposes to B_2O_3 and H_2O firstly. Then the RE oxide achieved in reaction 1 will react with boric oxide:

$$3RE_2O_3 + B_2O_3 \rightarrow 2RE_3BO_6 \tag{2}$$

After added more amount of H_3BO_3 , reaction (3) and (4) will take place:

$$RE_2O_3 + B_2O_3 \rightarrow 2REBO_3 \tag{3}$$



Fig. 1. XRD patterns of the samples (peaks of monoclinic phase, hexagonal phase, cubic phase are marked by "+", "#", "o", respectively).



Fig. 2. Emission spectra of the samples (excitation: 147 nm VUV).

$$2B_2O_3 + 2RE_3BO_6 \rightarrow 6REBO_3 \tag{4}$$

Luminescent spectra of the phosphors are illustrated in Fig. 2. As known to all, intensities of transitions between different J levels are dependent on symmetry of the local environment of Eu^{3+} [9]. When H₃BO₃ is 1.5, pure (Y,Gd,Eu)BO₃ crystal of vaterite structure has strong absorption in VUV region, and vaterite phase offers D_{3d} inversion symmetry site and T symmetry site for activator Eu^{3+} [12]. ${}^{5}D_{0}-{}^{7}F_{1}$ magnetic-dipole transition that obeys parity selection rule is allowed, which causes the phosphor to mainly exhibit strong line emission at 593 nm. Just as discussed above, distorted vaterite crystal of (Y.Gd,Eu)BO3 also leads to the emission due to ${}^{5}D_{0}-{}^{7}F_{2}$ electric-dipole transition that is rather high. Also the crystal field splits ${}^{5}D_{0}-{}^{7}F_{2}$ transition into two main lines at 611 and 626 nm. When the H₃BO₃ is decreased to about 1 mol, the crystal structure changes into certain amount of RE3BO6 monoclinic crystal mixed with hexagonal borate. Monocline crystal has low structure symmetry, that offers an uneven ambient to Eu^{3+} , so the ${}^{5}D_{0}-{}^{7}F_{2}$ transition caused line emissions at 615 and 619 nm that can be seen, especially the emission at 615 nm. It is the existence of this monoclinic phase that improves the color purity of the phosphor. When H_3BO_3 is less than 0.4, the main crystal structure is body centered cubic, the typical emission of 611 nm due to ${}^{5}D_{0}-{}^{7}F_{2}$ becomes the strongest line. The Eu³⁺ ions in C₂ sites lead to intense emission in 611 nm due to the ${}^{5}D_{0}-{}^{7}F_{2}$ transition [10]. Wei et al. [6] reported that the improvement of color purity in nano-sized YBO3:Eu is because surface defects in nanophosphor has increased the degree of disorder and lowered the local symmetry of Eu³⁺, thus increased transition probability of ${}^{5}D_{0}-{}^{7}F_{2}$. After checked in detail, the spectrum of sample 'a' in Ref. [6] is found to be very similar to that of the sample with 1.3 mol H₃BO₃ in this work. This similarity means that maybe there exists very small amount of RE₃BO₆ in their sample 'a' that leads to the color purity improvement.

CIE coordinates of samples are shown in Fig. 3, from which we can find that x values of the samples are increasing



Fig. 3. CIE coordinates of samples (excitation: 147 nm VUV).



Fig. 4. Relative brightness of the samples (excitation: 147 nm VUV).

while y values are decreasing with the increasing of mole ratio of H_3BO_3 . This result is coincident with that of emission intensities.

Relative brightness under excitation of 147 nm VUV of the samples is shown in Fig. 4, from which we can see that when H_3BO_3 is 1.3 mol, relative brightness is almost equal to that of pure ortho-borate, while those samples with H_3BO_3 less than 1.0 mol is decreasing with the cutting down of H_3BO_3 .

4. Conclusions

 Eu^{3+} activated borate phosphors with different crystal structures could be achieved by combustion method. Through adjustment of the amount of boric acid, crystal structure will transform among cubic, monoclinic, and hexagonal. And the strongest emission peak of the phosphors will change between line emission at 611 nm and line emission at 593 nm according to the above saying transformation of crystal structure. Chroma improved phosphor can be prepared by controlling amount of H₃BO₃ due to the appropriate existence of RE₃BO₆, while the luminescent brightness is almost equal to that of ortho-borate.

Acknowledgements

Financial support from the National Hi-Tech R&D Program of China (863 Program, No. 2002AA302604) and the National Natural Science Foundation of China (50372086) is gratefully acknowledged.

References

- Hajime Yamamoto, Problems and Progress in Display Phosphors, Phosphor Global Summit, Scottsdale, USA, 2003.
- [2] Shigeo Shionoya, Phosphor Handbook, CRC Press, 1998.
- [3] Weidong Zhuang, Xiangzhong Cui, Zhijian Yu, Huang Xiaowei, Influence of doping on the crystal structures and luminescent properties of aluminate phosphors for Plasma Display Panel, SID03, 2003.
- [4] C.R. Ronda, J. Lumin. 72-74 (1997) 49-54.
- [5] K.-S. Sohn, C.H. Kim, J.T. Park, H.D. Park, J. Mater. Res. 17 (12) (2002) 3201–3205.
- [6] Z. Wei, L. Sun, C. Liao, C. Yan, Appl. Phys. Lett. 80 (2002) 1447–1449.
- [7] Yu Zhijian, Zhuang Weidong, Huang Xiaowei, Wu Jie, Sheng Zhaokun, Han Junxiang, Proc. 2001' International Symposium on Nano-Materials and Technology, Beijing, China (2001).
- [8] J. Holsa, Inorgan. Chim. Acta 139 (1987) 257-259.
- [9] G. Blasse, B.C. Grabmaier, Luminescent Materials, Springer-Verlag, Heidelberg, Berlin, 1994.
- [10] M. Buijs, A. Meyerink, G. Blasse, J. Lumin. 37 (1987) 9-20.
- [11] X. Pingbo, D. Changkui, Z. Weiping, Y. Ming, L. Liren, X. Shangda, Chin. J. Lumin. 19 (2) (1998) 123–128.
- [12] G. Chadeyron, M. El-Ghozzi, R. Mahiou, A. Arbus, J.C. Cousseins, J. Solid State Chem. 128 (1997) 261–266.