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Preparation of red-emitting phosphor $(Y,Gd)BO_3:Eu^{3+}$ by high temperature ball milling

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Abstract

The red-emitting phosphor $(Y,Gd)BO_3:Eu^{3+}$ was prepared by high temperature ball milling in order to improve the color purity and decrease the calcining temperature. The phosphor was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and luminescence spectra. The results showed that the phosphor$(Y,Gd)BO_3:Eu^{3+}$ could be obtained at 600 °C, i.e. at a much lower temperature in contrast to conventional solid state reaction. The phosphor can be effectively excited by VUV radiation at 147 nm. In its emission spectrum, the strongest peak at 628 nm correlating to red emission was ascribed to the forced electric dipole transition $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} ions. Its chromaticity coordinates (CIE) were calculated to be $x=0.65$, $y=0.35$. Significantly, the intensity ratio of $Y_{0.65}Gd_{0.1}Eu_{0.25}BO_3$ phosphors of the red ($^5D_0 \rightarrow {}^7F_2$) to the orange ($^5D_0 \rightarrow {}^7F_1$) transition (*R*/*O* value) is 2.39, which is higher than 2.15 of the phosphor prepared by solid state reaction. The color purity was significantly improved. The particles with narrow distribution range and spherical morphology were approximately 200 nm in size. The luminescent properties of the $(Y,Gd)BO_3:Eu^{3+}$ sample with 25 mol% doping concentration of Eu^{3+} were optimal. Therefore, high temperature ball milling is of help to $(Y,Gd)BO_3:Eu^{3+}$ phosphor for improving the color purity and decreasing the calcining temperature in the future applications.

Keywords: YBO_3; Rare earth; High temperature ball milling; Phosphor

1. Introduction

Much attention has been paid to rare earth borates due to their ideal VUV absorption, stable physico-chemical properties and non-linear optical properties [1–3]. These have been widely used as phosphors for Plasma display panels (PDP) and Hg-free fluorescent lamps. The phosphor is one of the key factors affecting the performance of PDP devices, which can emit visible light under excitation with VUV 147 nm or 172 nm from Xe/He gas plasma. Thus the phosphors host lattice must absorb efficiently in the VUV range. The commercial red-emitting phosphor $(Y,Gd)BO_3$ doped with Eu^{3+} has been widely used in PDP for its high VUV absorption and thermodynamic stability, although its strongest emission peak is at 592 nm, corresponding to orange color light from $^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+} ions [4]. The $(Y,Gd)BO_3:Eu^{3+}$ phosphor is usually synthesized through conventional high temperature solid state reaction of about 1000 °C for 4–5 h, which can cause severe agglomeration [5]. And then, long time grinding is indispensable for the following process. As a result, the crystal lattice of phosphor is destroyed to some degree and the luminescent intensity greatly decreases. It is well known that the luminescent properties of a phosphor depend on the synthesis methods to a certain extent. The rare earth borates have been reported with a variety of synthesis methods, such as the hydrothermal [6,7], combustion [8], sol–gel [9,10], and the precipitation method [11,12], of these methods only solid state reaction is suitable for industrial production.

A new method named high temperature ball milling was invented [13]. In this work, $(Y,Gd)BO_3:Eu^{3+}$ was obtained by this new method at a much lower temperature compared to that in conventional high temperature solid state reaction.

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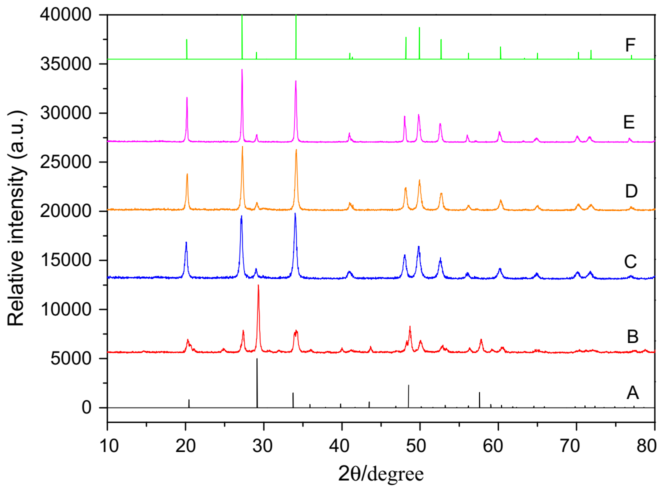

Fig. 1. XRD patterns of $Y_{0.8}Gd_{0.1}Eu_{0.1}BO_3$ phosphors prepared at different temperatures. A: standard pattern of Y_2O_3, B: 500 °C, C: 600 °C, D: 650 °C, E:700 °C, and F: standard pattern of YBO_3.

The as-prepared phosphor exhibits better red color purity with stronger emission intensity.

2. Experimental

The stoichiometric amounts of Y_2O_3 (99.99%), Gd_2O_3 (99.99%), Eu_2O_3 (99.99%) were dissolved in dilute HNO_3. Next, the solution was evaporated to dryness. Then, the stoichiometric amount of H_3BO_3 (A.R.) was added. The obtained mixture was ball-milled at 500–750 °C for 1–4 h, 1:15 weight ratio to the grinding balls.

The powder product was characterized by X-ray diffraction (XRD) (Rigaku D/max-2200) employing Cu Kα radiation ($\lambda = 0.154\ 18$ nm) at 40 kV and 20 mA. The luminescent properties under VUV excitation were measured using a fluorescence spectrophotometer (Edinburgh FLS-920T) with VM-504 vacuum monochromator, R928p photomultiplier tube (PMT) and a deuterium lamp as the excitation source. The morphology of the phosphor was observed on a Hitachi S-4800 scanning electron microscope (SEM) at an accelerating voltage of 15 kV. All the measurements were performed at room temperature.

3. Results and discussion

In the experiments, we regard $Y_{0.8}Gd_{0.1}Eu_{0.1}BO_3$ phosphors as an example to investigate the structure and fluorescence properties of $(Y,Gd)BO_3:Eu^{3+}$ phosphors. The XRD patterns of the obtained $Y_{0.8}Gd_{0.1}Eu_{0.1}BO_3$ phosphors at 500–700 °C for 2 h by high temperature ball milling and the standard patterns of Y_2O_3 and YBO_3 are shown in Fig. 1. From the XRD patterns shown in Fig. 1, the major peaks assigned to YBO_3 along with one impurity phase peak of Y_2O_3 ($2\theta = 29°$) were observed from the sample ball-milled at 500 °C. When the ball-milling temperature was increased to 600 °C or over, only the single phase of YBO_3, hexagonal system crystal structure, with space group $P6_3/m$, was observed and the impurity phase Y_2O_3 peaks disappeared. Compared with conventional high temperature solid state reaction [5], the reaction temperature utilized in high temperature ball milling can be decreased greatly because the mechanical energy and the heat are simultaneously transferred to the reactant.

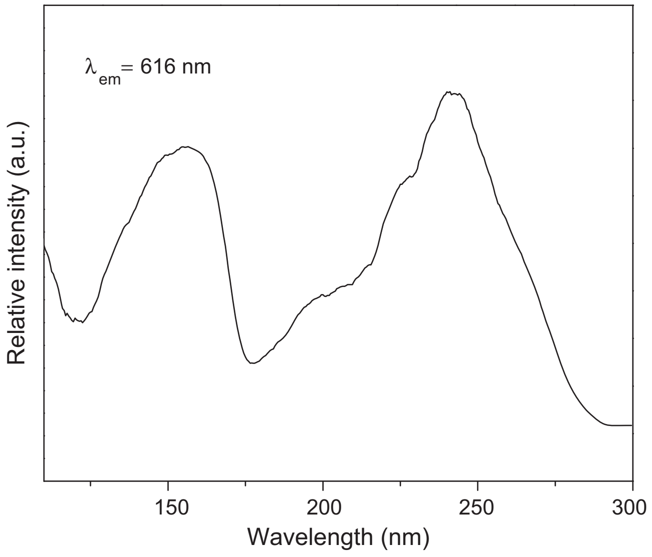

Fig. 2. The excitation spectra of $Y_{0.8}Gd_{0.1}Eu_{0.1}BO_3$ phosphor.

The 616 nm excitation spectrum of $Y_{0.8}Gd_{0.1}Eu_{0.1}BO_3$ phosphor is shown in Fig. 2. Two broad bands at around 150 nm and 250 nm are shown, the one around 130–170 nm arose from the host BO_3 group absorption, and another in the region of 200 nm to 280 nm were assigned to the charge transfer (CT) transition between Eu^{3+} ions and the neighboring O^{2-} ions, indicating that the $Y_{0.8}Gd_{0.1}Eu_{0.1}BO_3$ phosphor can effectively absorb vacuum ultraviolet light (147 nm) and ultraviolet light (254 nm), then emit red radiation. The phosphor emitting red at 147 nm and 254 nm easily meet VUV and UV absorption requirements in PDP and mercury-free fluorescent lamp applications, respectively.

The emission spectra of $Y_{0.8}Gd_{0.1}Eu_{0.1}BO_3$ prepared by high temperature ball milling at 700 °C for 2 h and solid state reaction at 1000 °C for 2 h under 147 nm excitation are shown in Fig. 3. The two spectra presented similar emission peaks, the peak at 594 nm radiation with orange color correlated to magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+} ions, while the red emission peaks at 613 nm and 628 nm were due to the forced electric dipole $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions. The other weaker peaks could be assigned to the $^5D_0 \rightarrow {}^7F_J$ ($J = 3$, 4, 5, and 6) transitions of Eu^{3+} ions. For the phosphor prepared by solid state reaction, the orange emission at 594 nm from transition of $^5D_0 \rightarrow {}^7F_1$ was dominant, but for the phosphor made with high temperature ball milling, the red emission at 628 nm from transition of $^5D_0 \rightarrow {}^7F_2$ was dominant. For the former, its intensity ratio of the red ($^5D_0 \rightarrow {}^7F_2$) to the orange ($^5D_0 \rightarrow {}^7F_1$) transition (*R*/*O* value) is 1.99, while the *R*/*O* value, for the latter, is 2.14. Both *R*/*O* values above suggest that the improved color purity can be obtained by high temperature ball-milling.

Fig. 4 shows the chromaticity coordinates of $Y_{0.8}Gd_{0.1}Eu_{0.1}BO_3$ phosphor. The chromaticity coordinates of phosphor

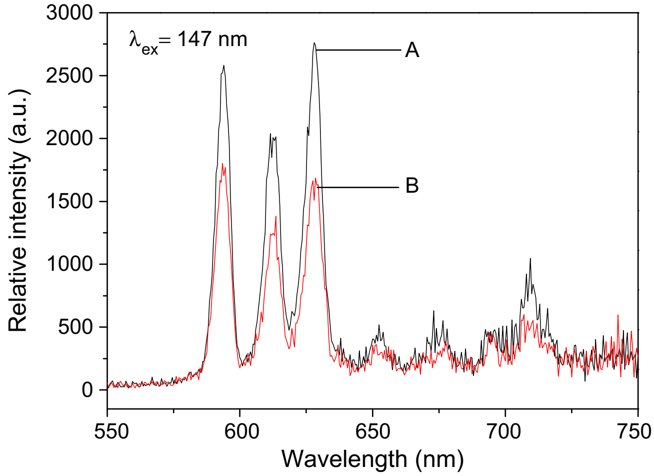

Fig. 3. The emission spectra of $Y_{0.8}Gd_{0.1}Eu_{0.1}BO_3$ phosphors prepared by different methods. A: high temperature ball milling and B: solid state reaction.

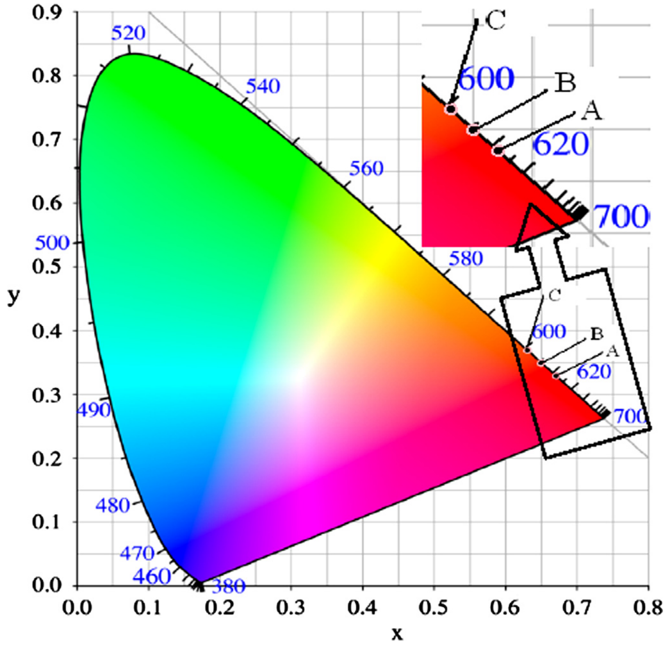

Fig. 4. Chromaticity coordinates of $Y_{0.8}Gd_{0.1}Eu_{0.1}BO_3$ phosphors. A: NTSC red, B: high temperature ball m1illing and C: solid state reaction.

$Y_{0.8}Gd_{0.1}Eu_{0.1}BO_3$ prepared by solid state reaction were calculated to be $x=0.63$, $y=0.37$. The coordinates of phosphor $Y_{0.8}Gd_{0.1}Eu_{0.1}BO_3$ prepared by high temperature ball milling were $x=0.65$, $y=0.35$, which are close to the standards set by the National Television Standard Committee (NTSC) ($x=0.67$, $y=0.33$). It is obvious that the color purity of phosphor prepared by high temperature ball milling was improved greatly.

The correlation between luminescent intensity and the ball milling temperature is shown in Fig. 5. The emission intensity of phosphor differed from different ball-milling temperatures. The emission intensity gradually increased with the increasing temperature in the range from 500 to 700 °C, reaching a maximum at 700 °C, and then started to decrease from 750 °C.

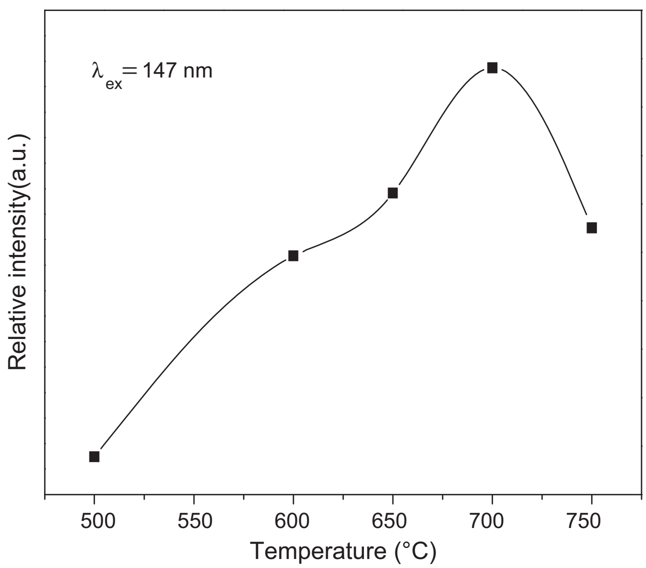

Fig. 5. The emission intensity of $Y_{0.8}Gd_{0.1}Eu_{0.1}BO_3$ at different ball-milling temperatures.

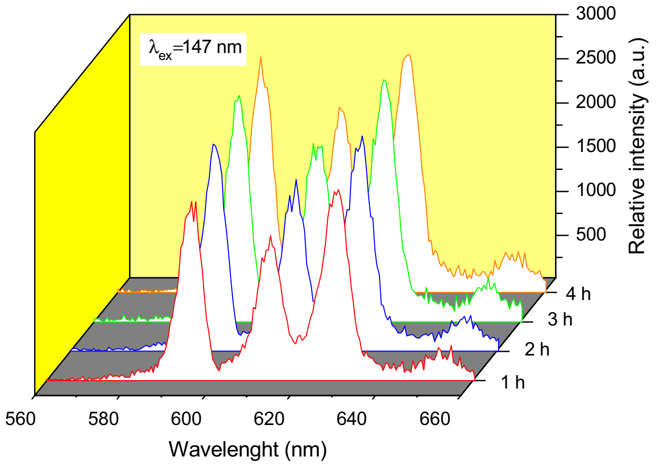

Fig. 6. The emission spectra of $Y_{0.8}Gd_{0.1}Eu_{0.1}BO_3$ with different ball-milling times.

In the experiments, 700 °C is the optimized ball milling temperature.

Fig. 6 shows the emission spectra of $Y_{0.8}Gd_{0.1}Eu_{0.1}BO_3$ phosphors at 700 °C with different ball milling times. As shown in Fig. 6, the emission intensities of $Y_{0.8}Gd_{0.1}Eu_{0.1}BO_3$ phosphors increase with ball milling times from 1 to 3 h, and then remain constant.

Fig. 7 shows the SEM images of the $Y_{0.8}Gd_{0.1}Eu_{0.1}BO_3$ phosphors prepared by high temperature ball-milling at 700 °C for 2 h and solid state reaction at 1000 °C for 2 h. It shows that the particles prepared by high temperature ball-milling were spherical shaped and homogeneously distributed, approximately 200 nm in size, while the phosphor particles prepared by solid state reaction were non-uniform in size with severe agglomeration.

From the XRD patterns of the $Y_{0.90-x}Gd_{0.10}Eu_xBO_3$ ($x\leq 0.30$) phosphors with different Eu^{3+} concentrations (unshown), these

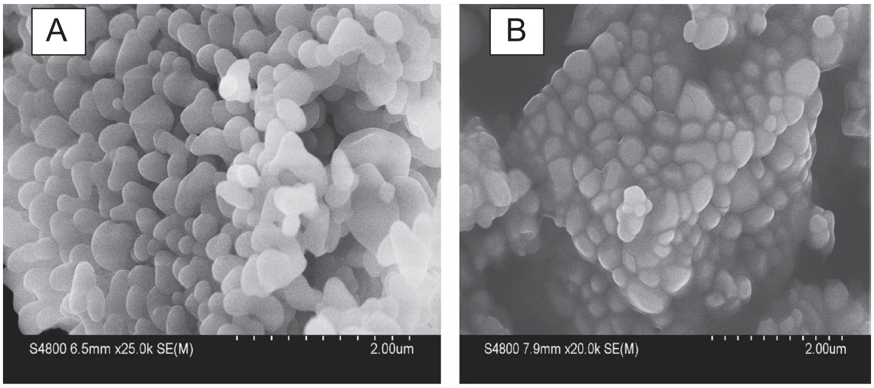

Fig. 7. SEM images of $Y_{0.8}Gd_{0.1}Eu_{0.1}BO_3$ phosphors prepared by different methods. A: high temperature ball milling and B: solid state reaction.

Table 1
Unit parameters of $Y_{0.9-x}Gd_{0.1}Eu_xBO_3$ ($x \leq 0.3$) phosphors.

x (mol%)	a (Å)	c (Å)	v (Å^3)
0	3.77	8.78	108.04
10	3.78	8.80	108.90
15	3.78	8.82	109.44
20	3.79	8.83	109.61
25	3.79	8.84	110.12
30	3.80	8.84	110.64

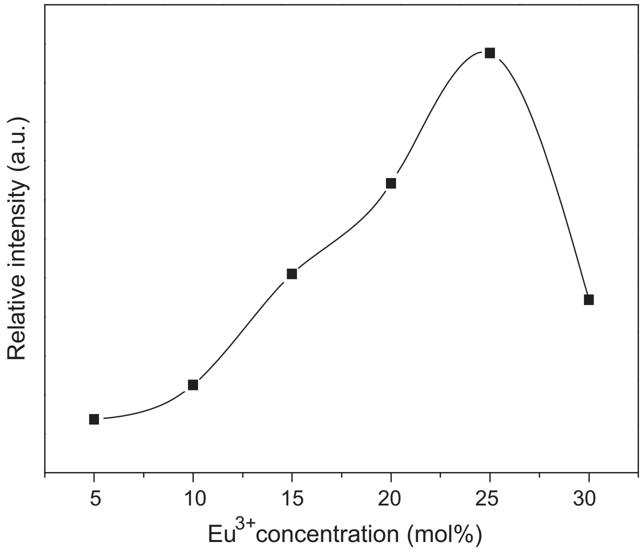

Fig. 8. The emission intensity of $Y_{0.90\text{-}x}Gd_{0.10}Eu_xBO_3$ with different Eu^{3+} doping molar ratios.

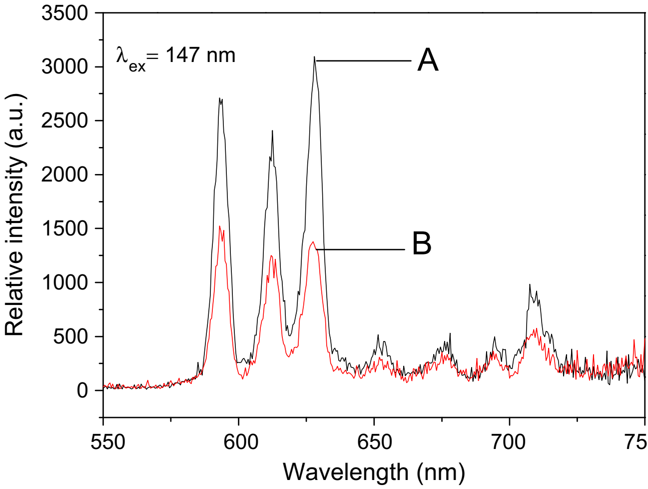

Fig. 9. The emission spectra of $Y_{0.65}Gd_{0.1}Eu_{0.25}BO_3$ phosphors prepared by different methods. A: high temperature ball milling and B: solid state reaction.

phosphors have the same crystalline structure. The wavelengths and intensities of the corresponding peaks are similar, belonging to the pure phase YBO_3, without other impurity phase peaks. According to the JCPDS Card #88-356, the $Y_{0.90-x}Gd_{0.10}Eu_xBO_3$ ($x \leq 0.30$) phosphors measured here had the hexagonal crystal structure with a space group of $P6_3/m$. The calculated unit cell parameters of $Y_{0.9-x}Gd_{0.1}Eu_xBO_3$ ($x \leq 0.3$) are shown in Table 1. The unit parameters a, c and v increased with the molar fraction of Eu^{3+} doped ions ($x \leq 0.3$). The structure of YBO_3 distorted to some degree when Y^{3+} (0.89 Å) ions are replaced with larger Eu^{3+} (0.95 Å) ions, so the increased unit cell parameters a, c and v in the YBO_3 lattice are obtained in Table 1.

Fig. 8 shows the Eu^{3+} doping concentration dependence of luminescent intensity of $Y_{0.90-x}Gd_{0.10}Eu_xBO_3$ ($x \leq 0.30$) phosphors, which are respectively excited by VUV light (147 nm). The intensities of the phosphors enhanced with the increase of the molar fraction of the doped Eu^{3+} and reached a maximum when it was 25%. Molar ratios over 25% led to concentration quenching.

Fig. 9 shows the emission spectra of $Y_{0.65}Gd_{0.1}Eu_{0.25}BO_3$ phosphors prepared by high temperature ball milling at 700 °C for 2 h and solid state reaction at 1000 °C for 2 h. The R/O values of $Y_{0.65}Gd_{0.1}Eu_{0.25}BO_3$ phosphors by high temperature ball milling and solid state reaction are 2.39 and 2.15, respectively, indicating that the color purity can be improved by high temperature ball-milling.

4. Conclusion

The red-emitting phosphors $(Y,Gd)BO_3:Eu^{3+}$ were successfully prepared by high temperature ball milling. The experimental results indicate that ball milling temperature is obviously lower than that by high temperature solid state reaction. Moreover, the phosphors can be effectively excited by VUV light at 147 nm, emitting bright red lights, which is due to the forced electric dipole transition $^5D_0 \rightarrow {}^7F_2$ of the doped Eu^{3+} ions. In particular, $Y_{0.65}Gd_{0.1}Eu_{0.25}BO_3$ phosphors show well color purity and optimal emission intensity. Therefore, high temperature ball milling is a well method, which can effectively improve $(Y,Gd)BO_3:Eu^{3+}$ phosphors the color purity and decrease their calcining temperature.

Acknowledgments

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References

[1] L.L. Wang, Y.H. Wang, Relationship between Eu^{3+}-doped borate phosphors properties and its crystal structure under vacuum ultraviolet excitation, J. Rare Earths 22 (2004) 863–867.

[2] R. Balakrishnaiah, S.S. Yi, K. Jang, H.S. Lee, Enhanced luminescence properties of $YBO_3:Eu^{3+}$ by Li-doping, Mater. Res. Bull. 44 (2009) 2228–2232.

[3] K. Park, J. Kim, K.Y. Kim, Enhancement of green emission for Al^{3+} doped $YBO_3:Tb^{3+}$, Mater. Chem. Phys. 136 (2012) 264–267.

[4] R.P. Rao, D.J. Devine, RE-activated lanthanide phosphate phosphor for PDP applications, J. Lumin. 1260 (2000) 87–89.

[5] X.Z. Cui, W.D. Zhuang, X.Y. Zhang, T. Xia, Z Long, Z.J. Yu, C.L. Zhao, X.W. Huang, Red emitting phosphor $(Y,Gd)BO_3:Eu^{3+}$ for PDP prepared by complex method, J. Rare Earths 24 (2006) 149–152.

[6] H. Ogata, S. Takeshita, Tetsuhiko Isobe, T. Sawayama, S. Niikura, Factors for determining photoluminescence properties of $YBO_3:Ce$ phosphor prepared by hydrothermal method, Opt. Mater. 33 (2011) 1820–1824.

[7] X.C. Jiang, L.D. Sun, C.H. Yan, Ordered nanosheet-based $YBO_3:Eu^{3+}$ assemblies: synthesis and tunable luminescent properties, J. Phys. Chem. B 108 (2004) 3387–3390.

[8] Z.J. Yu, X.W. Huang, W.D. Zhuang, X.Z. Cui, H.W. Li, Crystal structure transformation and luminescent behavior of the red phosphor for plasma display panels, J. Alloys Compd. 390 (2005) 220–222.

[9] D. Boyer, G. Bertrand, R. Mahiou, A spectroscopic study of vaterite form $YBO_3:Eu$ processed by sol–gel technique, J. Lumin. 104 (2003) 229–237.

[10] Z.G. Wei, L.D. Sun, C.S. Liao, J.L. Yin, X.C. Jiang, C.H. Yan, Size-dependent chromaticity in $YBO_3:Eu$ nanocrystals: Correlation microstructure and site symmetry, J. Phys. Chem. B 106 (2002) 10610–10617.

[11] X.Z. Cui, W.D. Zhuang, Z.J. Yu, X.W. Huang, H.W. Li, Preparation of red phosphor $(Y,Gd)BO_3:Eu$ by soft chemistry methods, J. Alloys Compd. 451 (2008) 280–285.

[12] A.E. Henkes, R.E. Schaak, Synthesis of nanocrystalline $ReBO_3$ (Re = Y, Nd, Sm, Eu, Gd, Ho) and $YBO_3:Eu$ using borohydride-based solution precursor route, J. Solid State Chem. 181 (2008) 3264–3268.

[13] Z.B. Shao, Q.W. Hao, Z.C. Shao, K.R. Liu, ZL 200610047610.8, 2009.