J Mater Sci (2008) 43:2908–2911
DOI 10.1007/s10853-007-1805-5

Luminescence properties of $Y_{0.95-x}M_xEu_{0.05}B_{1-y}R_yO_3$ (M = Ca, Sr, Ba, Zn, Al, $0 \leq x \leq 0.1$; R = Si, P, $0 \leq y \leq 0.1$) in UV and VUV regions

Lingli Wang · Yuhua Wang

Received: 1 February 2007 / Accepted: 24 April 2007 / Published online: 3 July 2007

Abstract The phosphors $Y_{0.95-x}M_xEu_{0.05}B_{1-y}R_yO_3:Eu^{3+}$ (M = Ca, Sr, Ba, Zn, Al, $0 \leq x \leq 0.1$; R = Si, P, $0 \leq y \leq 0.1$) are successfully synthesized by solid-state reaction. All the solid samples are identified as isomorphs. Their luminescent properties are studied under UV and VUV excitation. With the incorporation of metallic or nonmetallic cations, the chromaticity of $YBO_3:Eu^{3+}$ is remarkably improved as well as the luminescent intensity increased. When 10% of Al^{3+} is doped into YBO_3 host lattice, the best ratio of the red emission at 610 nm to the orange one at 591 nm is obtained and the luminescent intensity increased simultaneously. The reason is analyzed, and can be explained by the decrease of the symmetry around Eu^{3+} site in YBO_3 host lattice.

Introduction

Over the last few years, more and more attention has been focused on plasma display panels (PDPs). It is regarded as the most promising candidates for large sized flat panel displays (FPD) [1]. Tricolor inorganic luminescent materials are used in PDP to emit red, green and blue light. Both high luminescent efficiency and good color purity are required for PDP and Hg-free lamp phosphors. As far as red phosphor is concerned, $(Y,Gd)BO_3:Eu^{3+}$ is widely used today, but its main emission peak is at about 591 nm, leading to a poor chromaticity [2]. In order to achieve a good picture quality, the search for improving current phosphors or developing new red PDP phosphors is urgently required.

The pure red emission, which can be obtained from $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} is hypersensitive to the lattice symmetry of the host crystal and will be relatively strong if the symmetry of the crystal is low, this is consistent with Judd-Ofelt theory [3]. The Eu^{3+} ions in $(Y,Gd)BO_3:Eu^{3+}$ Occupy an inversion symmetry, so the transition of $^5D_0 \rightarrow {}^7F_1$ (591 nm) is predominated. Accordingly, $YBO_3:Eu^{3+}$ nanocrystals are prepared to improve the chromaticity, but the luminescent efficiency is reduced greatly at the same time [4]. Recently, much research has been done to find new red phosphors [5–8], whereas their luminescent efficiency is not satisfied. We try to solve the chromaticity disadvantage of $(Y,Gd)BO_3:Eu^{3+}$ and improve the luminescent efficiency at the same time. Introducing other atoms into orthoborate host may be an interesting method to reduce its crystal symmetry. Elements such as Ca, Sr, Ba, Zn, Al, Si, P are selected as dopants because of their wide application in luminescent host materials. Due to their different ionic radius from that of Y or B ion, the crystal lattice can be disordered, and the high symmetry around Eu^{3+} site can be destroyed.

In this paper, $Y_{0.95-x}M_xEu_{0.05}B_{1-y}R_yO_3:Eu^{3+}$ (M = Ca, Sr, Ba, Zn, Al, $0 \leq x \leq 0.1$; R = Si, P, $0 \leq y \leq 0.1$) are prepared by solid-state reaction. Their luminescent properties are investigated under UV and VUV region. The effects of the codopants on the luminescent properties are evaluated and explained.

Experiments

The starting materials are Y_2O_3, Eu_2O_3 (99.99%), Al_2O_3 (99.5%), ZnO, $CaCO_3$, $SrCO_3$, $BaCO_3$ (99.0%), SiO_2

L. Wang · Y. Wang (✉)
Department of Material Science, School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, P.R. China
e-mail: wyh@lzu.edu.cn

(98.5%), $(NH_4)_2HPO_4$ and H_3BO_3 (99.5%). Powder samples of $Y_{0.95-x}M_xEu_{0.05}B_{1-y}R_yO_3{:}Eu^{3+}$(M = Ca, Sr, Ba, Zn, Al, $0 \le x \le 0.1$; R = Si, P, $0 \le y \le 0.1$) are prepared by heating the mixture of the starting materials in appropriate ratio in air. After intimately mixing these powders with ethanol, the mixture is heated at 500 °C for 2.5 h, reground, and again heated at 1,100 °C for 3 h.

All the samples are characterized by powder X-ray diffraction (XRD) using a Rigaku diffractometer with Ni-filtered CuKα radiation at room temperature. The luminescent properties under ultraviolet (UV) excitation are measured by a Hitachi F-4500 fluorescence spectro-photo-meter. And that under vacuum ultraviolet (VUV) excitation are measured with an ARC model VM-502-type vacuum mono-chromator with a deuterium lamp. The VUV excitation spectra are corrected by dividing the excitation intensity of sodium salicylate at the same measurement conditions. All the luminescent spectra are recorded at room temperature.

Results and discussion

All the powder samples of $Y_{0.95-x}M_xB_{1-y}R_yO_3$ (M = Ca, Sr, Ba, Zn, Al, $0 \le x \le 0.1$; R = Si, P, $0 \le y \le 0.1$) doped with 5% (mol fraction) Eu^{3+} appear to be white color in body. The X-ray powder diffraction patterns of $Y_{0.95-x}M_xEu_{0.05}B_{1-y}R_yO_3{:}Eu^{3+}$(M = Ca, Sr, Ba, Zn, Al, $0 \le x \le 0.1$; R = Si, P, $0 \le y \le 0.1$) calcined at 1,100 °C for 3 h are recognized as single phases. As an example, Fig. 1 displays the XRD patterns of $Y_{0.95-x}Eu_{0.05}Al_xBO_3$ ($0 \le x \le 0.1$). They can be recognized as single phase in terms of JCPDF (16-0277), and there is no second phase observed, for example, $Y_{0.85}Eu_{0.\ 05}Al_{0.10}BO_3$ is easily indexed to a hexagonal system with the lattice parameters $a = 0.\ 37762(2)$, $c = 0.87954(2)$ nm.

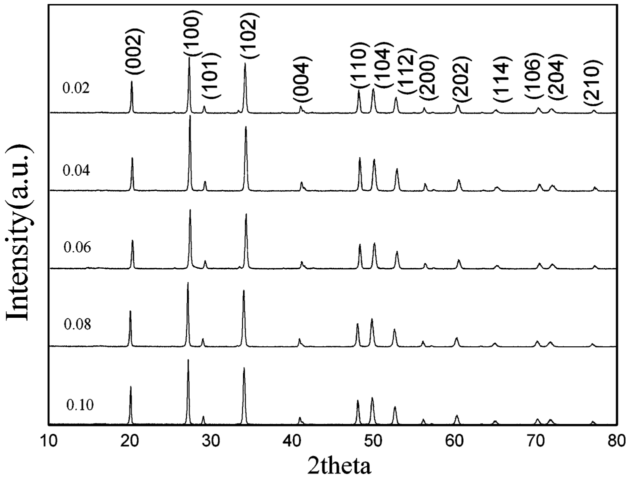

Fig. 1 XRD patterns of $Y_{0.95-x}Eu_{0.05}Al_xBO_3$ ($0 \le x \le 0.1$) prepared by solid-state reaction

The emission spectra of $Y_{0.95-x}M_xEu_{0.05}B_{1-y}R_yO_3{:}Eu^{3+}$(M = Ca, Sr, Ba, Zn, Al, $0 \le x \le 0.1$; R = Si, P, $0 \le y \le 0.1$) and $Y_{0.95}Eu_{0.05}BO_3$ under 254 nm irradiation are shown in Fig. 2(a). The results indicate that all the emission spectra are similar and three sharp lines at about 591, 610 and 627 nm are observed, which can be assigned to the transitions from the excited $^5D_0$ level to ^7F_J (J = 1, 2,) levels of Eu^{3+} [9, 10]. The relative intensity of $^5D_0 \rightarrow {}^7F_2$ emission depends strongly on the local symmetry of Eu^{3+} site, and a lower symmetry of crystal lattice around Eu^{3+} ions will induce a higher R/O (the ratio of the red emission at 610 nm to the orange one at 591 nm) value. As can be seen from Fig. 2(a), the ratio of the red emission at 610 nm to the orange one at 591 nm of

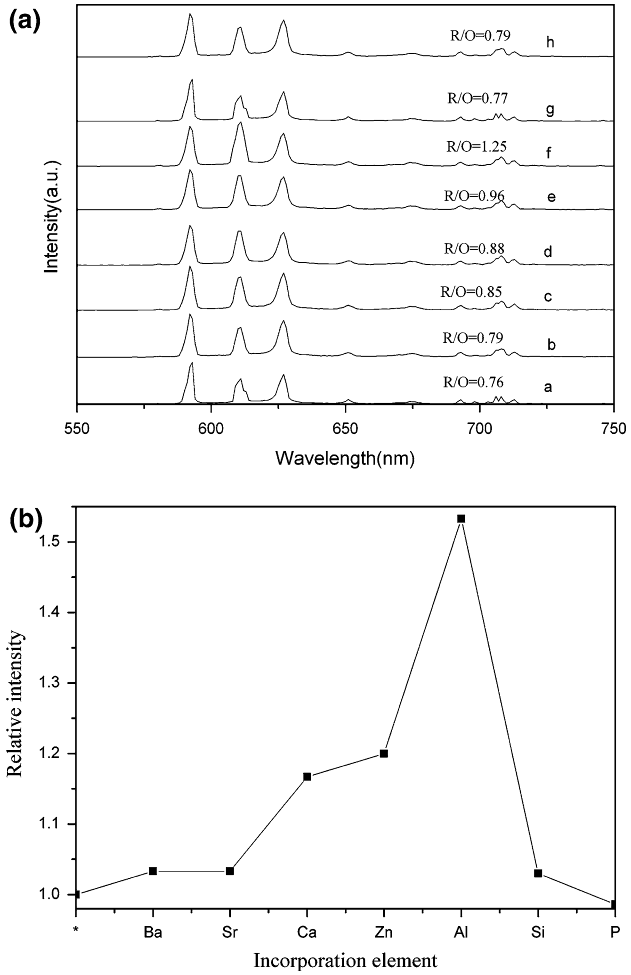

Fig. 2 (**a**) Emission spectra of $Y_{0.95-x}M_xEu_{0.05}B_{1-y}R_yO_3{:}Eu^{3+}$(M = Ca, Sr, Ba, Zn, Al, $x = 0.1$; R = Si, P, $y = 0.1$) under 254 nm excitation for samples with different do pants: $Y_{0.95}Eu_{0.05}BO_3$ (a), 10%Ba (b), 10%Sr (c), 10% Ca (d), 10%Zn (e), 10%Al (f), 10%P (g) and 10%Si (h); (**b**) The change of the luminescent intensity of $YBO_3{:}5\%Eu^{3+}$ with different incorporation ions

$Y_{0.95-x}$ $M_xEu_{0.05}B_{1-y}R_yO_3$:$Eu^{3+}$(M = Ca, Sr, Ba, Zn, Al, $x = 0.1$; R = Si, P, $y = 0.1$) is much higher than that of $Y_{0.95}Eu_{0.05}BO_3$, and the best improvement of R/O is obtained when Al^{3+} is co-doped. Different disorder level of the YBO_3 lattice is caused by the co-do pants, resulting from their different ion radius. The lower the symmetry of Eu^{3+} site, the better chromaticity can be achieved. The R/O increases (0.79, 0.85, 0.88, 0.96, 1.25) with the decrease of the ion radius of the dopants ($\gamma_{Ba^{2+}} > \gamma_{Sr^{2+}} > \gamma_{Ca^{2+}} > \gamma_{Zn^{2+}}\ \gamma_{Al^{3+}}$), while the contrary result R/O = 0.77 or 0.79 is observed when B^{3+} ion is substituted by P^{5+} or Si^{4+}. The experiment results agree well with the theory, the transition probability and emission intensities of the various transitions are governed by selection rules and symmetry considerations of the site in which Eu^{3+} ion is presented. Fig. 2(b) shows the change of the luminescent intensity of YBO_3: 5%Eu^{3+} with different incorporation ions. Generally, the luminescent efficiency of phosphors will be lowered if some co-doped ions are introduced into the host lattice. It is true for Sr^{2+}, Ba^{2+}, Si^{4+} and P^{5+}, and this can be attributed to various pathways of nonradiative relaxation caused by the incorporation. While for Ca^{2+}, Zn^{2+} and Al^{3+} whose radii are smaller than that of Y^{3+}, the luminescent intensity of Eu^{3+} is enhanced. Similar phenomenon is observed in other systems [11]. The incorporation of smaller ions into the host lattice can help enhance the charge transfer (CT) excitation band of Eu^{3+} and the absorption band of the host lattice, and then higher emission of Eu^{3+} can be obtained.

Figure 3 displays the emission spectra of $Y_{0.95-x}Al_x$ BO_3:5%Eu^{3+} under 254 nm radiation, all the spectra are normalized with the peak at 591 nm in order to compare the relative intensity between different peaks. From Fig. 3, we can observe the concentration-dependent characteristic of R/O value. The R/O values are enhanced with the increase of Al^{3+} concentration, indicating a higher concentration of Al^{3+} ion is favorable to achieve superior chromaticity. The highest R/O value is achieved with the concentration of Al^{3+} ion of 10%. The x-dependent PL behavior indicates that a higher level of disorder can be obtained when x increases, and the R/O value is improved as well.

The luminescent properties $Y_{0.95-x}M_xEu_{0.05}B_{1-y}R_y$ O_3:Eu^{3+}(M = Ca, Sr, Ba, Zn, Al, $0 \leq x \leq 0.1$; R = Si, P, $0 \leq y \leq 0.1$) under 147 nm excitation are similar to that under 254 nm excitation. The spectra had a little difference from that under 254 nm excitation, the emission at about 627 nm is much higher than that at 610 nm, so the R/O value is defined as the ratio of the red emission at 627 nm to the orange one at 591 nm. As shown in Fig. 4, the R/O values for $Y_{0.95}Eu_{0.05}BO_3$ and that of $Y_{0.95}Eu_{0.05}BO_3$ with the incorporation of Ca, Sr, Ba, Zn, Al, P, and Si are 0.91, 0.89, 0.90, 0.91, 0.95, 1.2, 0.89 and 0.93, respectively. The better chromaticity is favorable to be obtained with smaller radii of the co-doping ions. Same to that under UV excitation, the best chromaticity is achieved when 10% Al^{3+} is co-doped into the host lattice. Figure 5 shows the emission spectra of $Y_{0.85}Eu_{0.05}Al_{0.1}BO_3$:$Eu^{3+}$ and $Y_{0.95}Eu_{0.05}BO_3$ under 147 nm excitation. As we can see, the R/O as well as luminescent intensity of $Y_{0.85}Al_{0.1}BO_3$:5%Eu^{3+} is higher than that of $Y_{0.95}Eu_{0.05}BO_3$. The chromaticity coordinates of $Y_{0.95}Eu_{0.05}BO_3$ is reported as $x = 0.645$, $y = 0.355$ and that of $Y_{0.85}Al_{0.1}BO_3$:5%Eu^{3+} is calculated to be $x = 0.654$, $y = 0.348$.

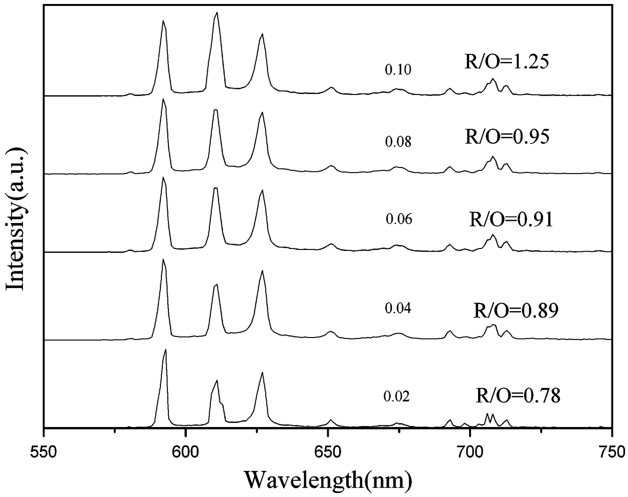

Fig. 3 Emission spectra of $Y_{0.95-x}Eu_{0.05}Al_xBO_3$ under 254 nm irradiation for samples with different aluminum ion concentration. All of them are normalized with the peak at 591 nm

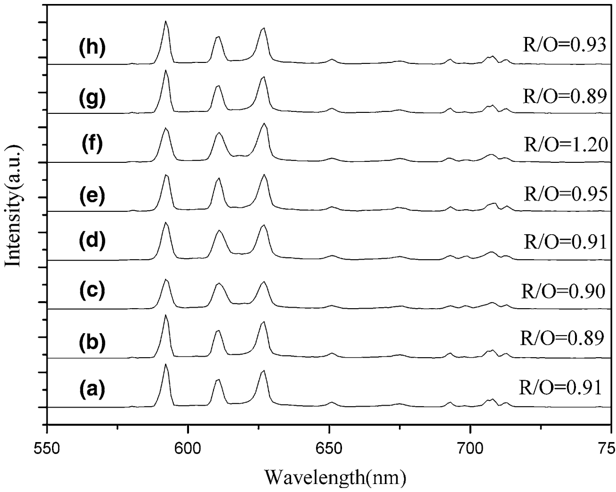

Fig. 4 Emission spectra of $Y_{0.95-x}M_xEu_{0.05}B_{1-y}R_yO_3$:$Eu^{3+}$(M = Ca, Sr, Ba, Zn, Al, $x = 0.1$; R = Si, P, $y = 0.1$) under 147 nm excitation for samples with different dopants: $Y_{0.95}Eu_{0.05}BO_3$ (**a**), 10%Ba (**b**), 10%Sr (**c**), 10% Ca (**d**), 10%Zn (**e**), 10%Al (**f**), 10%P (**g**) and 10%Si (**h**)

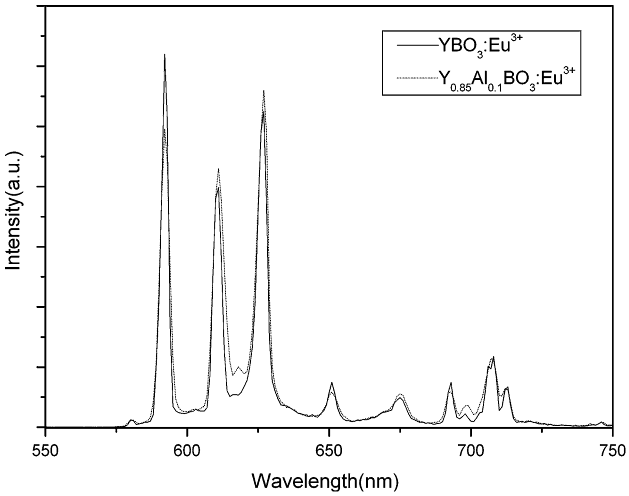

Fig. 5 Emission spectra of $Y_{0.85}Al_{0.1}BO_3$:5%Eu^{3+} and $Y_{0.95}Eu_{0.05}BO_3$ under 147 nm excitation

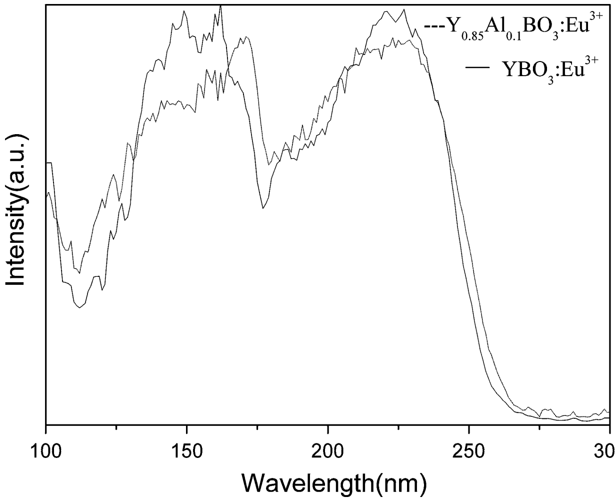

Fig. 6 Excitation spectra of the luminescence of $Y_{0.95}Eu_{0.05}BO_3$ and $Y_{0.85}Al_{0.1}BO_3$: 5%Eu^{3+}

The excitation spectra of $Y_{0.85}Al_{0.1}BO_3$:5%Eu^{3+} and that of $Y_{0.95}Eu_{0.05}BO_3$ are exhibited in Fig. 6. Two main broad bands with maxima at 160 and 230 nm are observed in the excitation spectra. According to Ref. [12], the broad band at about 230 nm is assigned to the CT band of Eu^{3+}–O^{2-} resulting from an electron transfer from the ligand $O^{2-}(2p^6)$ orbitals to the empty states of $4f^6$ for Eu^{3+} configuration. The band at about 160 nm is assigned to the absorption of the host lattice [13]. The intensity of the excitation bands of $Y_{0.85}Al_{0.1}BO_3$:5%Eu^{3+} is much higher than that of $Y_{0.95}Eu_{0.05}BO_3$ which is corresponding to the high luminescent intensity of $Y_{0.85}Al_{0.1}BO_3$:5%Eu^{3+}.

Conclusion

$Y_{0.95-x}M_xEu_{0.05}B_{1-y}R_yO_3$:$Eu^{3+}$(M = Ca, Sr, Ba, Zn, Al, $0 \le x \le 0.1$; R = Si, P, $0 \le y \le 0.1$) are synthesized by the traditional solid-state reaction and their luminescent properties are studied under UV and VUV excitation. The emission spectra show that the pure red emission from $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} is improved with the incorporation of Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Al^{3+}, Si^{4+} or P^{5+} into the host lattice of YBO_3:Eu^{3+}, leading to a better color purity. The luminescent intensity is also increased when Ca^{2+}, Zn^{2+}, Al^{3+} are introduced. $Y_{0.85}Al_{0.1}BO_3$:5%Eu^{3+} shows the best chromaticity and highest luminescent intensity, it would be the most promising red component in PDPs.

Acknowledgements We would like to thank the Ministry of Science and Technology of China 863 program (2003AA324020), the NSFC (50272026) and EYTP (Excellent Young Teachers Program of M0E, P.R.C.) for the financial support.

References

1. Shinoda T (2004) ASID'04, Proceedings of The 8th Asian Symposium on information Display, 1
2. Tian L, Yu BY, Pyun CH, Park HL, Mho SI (2004) Solid State Commun 129:43
3. Judd BR (1962) Phys Rev 127:750
4. Jiang X-C, Yan C-H, Sun L-D, Wei Z-G, Liao C-S (2003) J Solid State Chem 175:245
5. Wang YH, Uheda K, Takizawa H, Mizumoto U, Endo T (2001) J Electrochemical Soc 148(8):G430
6. Yoshimatsu R, Yoshida H, Minamoto M, Nishikage Y (2003) Proc Annu Conf Illuminating Eng Inst Jpn 36:13
7. Wu XY, You HP, Cui HT, Zeng XQ, Hong GY, Kim CH, Pyun CH, Yu BY, Park CH (2003) Mater Res Bull 37:1531
8. Wang Y, Endo T, Xie E, He D, Liu B (2004) Microelectronics J 35:357
9. Wegh RT, Donker H, Oskam KD, Meijerink A (1999) Science 283:663
10. Feldmann C, Jüstel T, Ronda CR, Wiechert DU (2001) J Lumin 92:245
11. Tian L, Mho Sun-il, Yu B-Y, Pyun C-H (2004) J Soc Inf Dis 12:517
12. Blasse G, Brill A (1966) Philips Res Rep 22:2356
13. Wang Y, Guo X, Endo T, Murakami Y, Ushirozaw M (2004) J Solid State Chem 177:2242