

Luminescent properties of $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors

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$\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors were fabricated by the sol-gel method. The structure properties were measured by x-ray diffraction (XRD) and infrared spectra (IR). Doping concentration of Eu^{3+} ions in $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors of 0, 1, 3, 4, and 5 mol% were studied. The excitation spectra and emission spectra of $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors were examined by fluorescent divide spectroscopy (FDS). The luminescent properties of $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors are discussed. The optimal doping concentration of Eu^{3+} ions in $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors was found to be approximately 3 mol%. © 2006 Springer Science + Business Media, Inc.

1. Introduction

The luminescent materials used in plasma display panels (PDPs) strongly resemble phosphors used in fluorescent lamps. PDPs are regarded as the most promising candidates for large area flat panel displays (FPD) [1–6]. For PDP applications, the phosphors are required to have high conversion efficiency by VUV radiation of 148 and 172 nm versus 185 and 254 nm in fluorescent lamps. The luminescence of the rare earth ions in inorganic hosts has been extensively investigated during the last few decades [7–10]. At present, the most widely used red-emitting phosphor for PDP is $(\text{Y,Gd})\text{BO}_3:\text{Eu}^{3+}$. However, the colorimetric purity of $(\text{Y,Gd})\text{BO}_3:\text{Eu}^{3+}$ is not sufficient to produce a high quality color TV picture. Some compounds with aluminate groups and borate groups have demonstrated strong absorption in the VUV region, so the aluminoborate family were investigated. In this paper, $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors were prepared by sol-gel method. The structure and luminescent properties are researched by X-ray diffraction (XRD), infrared spectroscopy (IR), and fluorescent divide spectroscopy (FDS). The luminescent properties in VUV region will be discussed in a later paper.

2. Experimental

$\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors were fabricated by the sol-gel method. The starting materials were $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

(AR), H_3BO_3 (AR), Y_2O_3 (99.95% purity), Eu_2O_3 (99.95% purity) and HNO_3 . Y_2O_3 and Eu_2O_3 were dissolved in HNO_3 and deionized water to form the solution, then stoichiometric amounts of $\text{Al}(\text{NO}_3)_3$ and H_3BO_3 were added and stirred to the solution to form a white sol under heat treatment. The sol was dried at 90°C for 15 hr to produce the $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ precursor. The precursor was calcined at various temperatures in air for 4 h to convert the $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphor to the desired crystal structure. The doping concentrations of Eu^{3+} ions of 1, 3, 4, and 5 mol% were studied.

The structure properties and luminescent properties of $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors particles were examined by X-ray diffraction (XRD), infrared spectroscopy (IR) and fluorescent divide spectroscopy (FDS) under an ultraviolet excitation source using a Hitachi F-4000 spectrometer.

3. Result and discussion

Fig. 1 contains the XRD plots of $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ (3 mol%) phosphors calcined at different temperatures. As shown in Fig. 1a and b, calcination temperatures of 700°C and 800°C are too low to convert the $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors to the desired crystal structure. When calcined at 900°C for 2 h, the XRD data for $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors in Fig. 1c matches the standard XRD card of $\text{YAl}_3(\text{BO}_3)_4$ compound. $\text{YAl}_3(\text{BO}_3)_4$ is known to have a

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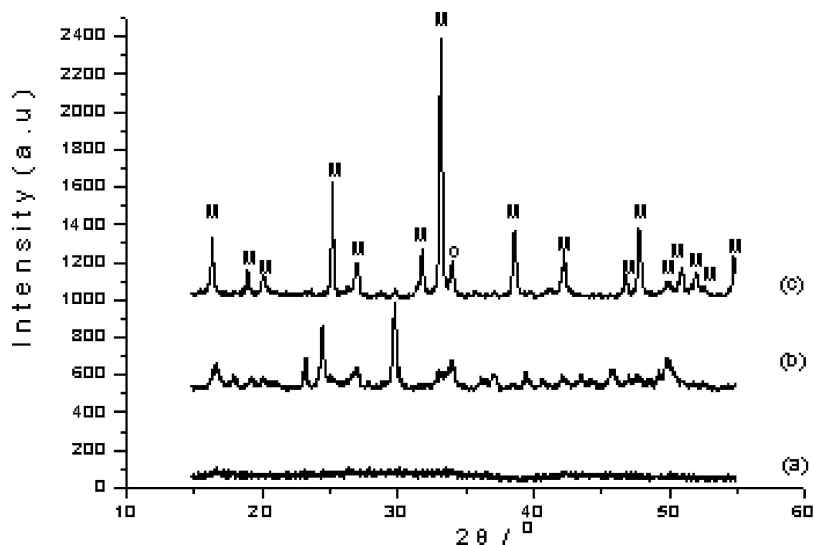


Figure 1 XRD patterns of $\text{YAL}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ (3 mol%) phosphors calcined at (a) 700°C, (b) 800°C, and (c) 900°C.

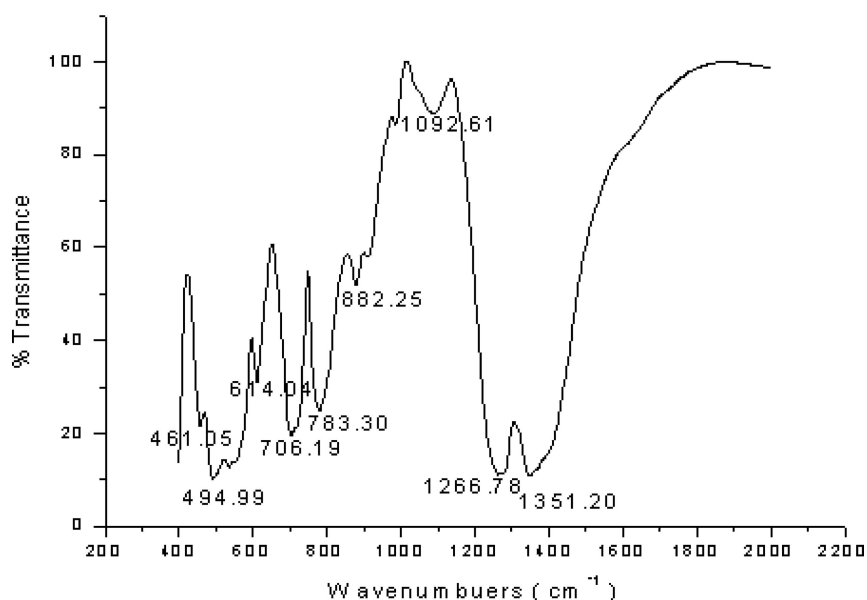


Figure 2 Infrared spectra of $\text{YAL}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ (3 mol%) phosphors.

rhombohedral symmetry with the space group R32, where the rare earth ions are at the center of distorted trigonal prism, which are non-centrosymmetric sites. The rare earth ion is situated at the origin with D_3 symmetry. The Y ionic radius is 0.089 nm and the rare earth ions can substitute Y^{3+} ions, located in trigonal prism sites, without causing any symmetry distortion. Furthermore, the neighboring Y -positions are separated by a large distance (~ 0.6 nm), due to the presence of the $(\text{BO}_3)^{3-}$ groups, which may screen the rare earth interactions even at high dopant concentrations.

Fig. 2 is the infrared spectra of the $\text{YAL}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ (3 mol%) phosphors. The spectra bands in the regions of 855–898 cm^{-1} , 655–755 cm^{-1} , and 601–655 cm^{-1} may belong to the curved vibrations of the O–B–O bond, while the bands at 1019–1148 cm^{-1} and 1212–1414 cm^{-1}

may be due to the stretch vibrations of B–O bond [11]. Typically, the adsorption of the stretch vibrations of the reverse symmetry of BO_3 occurs at 1100–1400 cm^{-1} while the adsorption of BO_4 occurs at 1100–1500 cm^{-1} . The stronger adsorption in the region of 1212–1414 cm^{-1} in Fig. 2 is representative of the stretch vibrations of the reverse symmetry of BO_3 , and the weaker adsorption in the region of 1019–1148 cm^{-1} is due to the stretch vibrations of reverse symmetry of BO_4 . Therefore, the boron elements exist in the form of BO_3 . Meanwhile, the adsorption of AlO_6 occurs in the range of 650–450 cm^{-1} . These IR results show that the sample prepared is $\text{YAL}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ and is consistent with the XRD data.

Fig. 3 is the excitation spectra of $\text{YAL}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ (3 mol%) phosphors doped with different amount of Eu^{3+} ions. The excitation wavelength is 615 nm. Rare

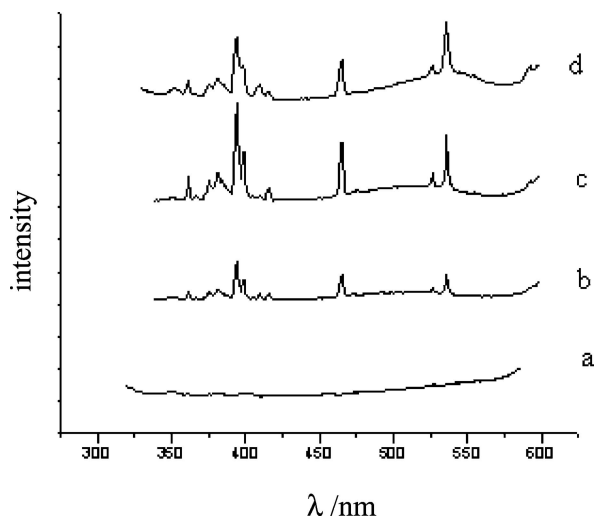


Figure 3 The excitation spectra of $\text{YAL}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors doped with (a) 0 mol%, (b) 1 mol%, (c) 3 mol%, and (d) 5 mol% Eu^{3+} ions.

earth ions in oxides are energetically preferred as the trivalent state. Their $4f^n$ valance electrons are shielded by the $5s^2p^6$ electrons. Due to this electron configuration, a sharp line due to the f-f transitions is observed in the optical absorption and fluorescence spectra [12]. In general, the luminescence of rare earth doped systems is dictated by the dopant properties. The adsorptions at 416 nm, 466 nm, 523 nm result from the ${}^7F_1 \rightarrow {}^5D_0$, ${}^7F_2 \rightarrow {}^5D_0$ and ${}^7F_3 \rightarrow {}^5D_0$ transitions, respectively. The adsorption at 396 nm from the ${}^7F_0 \rightarrow {}^5L_6$ transition is the strongest in results in Fig. 3. The doping amounts of Eu^{3+} ions in the phosphors are 0 mol%, 1 mol%, 3 mol% and 5 mol% in Fig. 3A–D, respectively. From Fig. 3, the relative intensity of the luminescence of $\text{YAL}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors is largest at

3 mol% doping, suggesting that this is near the optimum doping amount of Eu^{3+} ions in $\text{YAL}_3(\text{BO}_3)_4:\text{Eu}^{3+}$.

Fig. 4 is a plot of the emission spectra of $\text{YAL}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors doped with different amount of Eu^{3+} ions. There are four emission peaks at 591, 595, 613 and 617 nm, of which the emission peak at 613 nm is the strongest. The emission peaks at 591 nm and 595 nm result from the transition from ${}^5D_0 \rightarrow {}^7F_1$, while the others at 614 (613?) nm and 617 nm are due to the transition from ${}^5D_0 \rightarrow {}^7F_2$, induced by the lack of inversion symmetry at the Eu^{3+} site. The choice of host lattices for Eu^{3+} ion activator is very important, because the luminescent properties depend to a great extent on the site symmetry occupied by the Eu^{3+} ion, as discussed earlier. The Eu^{3+} ion replaces the Y^{3+} ion in both $\text{YAL}_3(\text{BO}_3)_4$. Y atoms are surrounded by eight oxygen atoms in an arrangement which can be described as a trigonal bicapped antiprism, where the Y^{3+} ion is in centrosymmetric sites. As a new host lattice for the Eu^{3+} activator for PDP applications, $\text{YAL}_3(\text{BO}_3)_4$ with trigonal space distorted R32 adopts the normal trigonal huntite type structure with Y-centered distorted trigonal prisms and Al-centered distorted octahedral dispersed between planes of BO_3 triangles that extend parallel to (001). Dissimilar polyhedra share only vertices, resulting in isolation of the YO_6 trigonal prisms and BO_3 triangles; AlO_6 octahedral share edges to form helices extending along (001).

The relative luminescent intensity of $\text{YAL}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors is largest when the doping concentration of Eu^{3+} ions is 3 mol%. The result is in accordance with the excitation spectra of $\text{YAL}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors. Therefore, it can be concluded that optimal doping concentration of Eu^{3+} ions in $\text{YAL}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors is between 1 and 4 mol%.

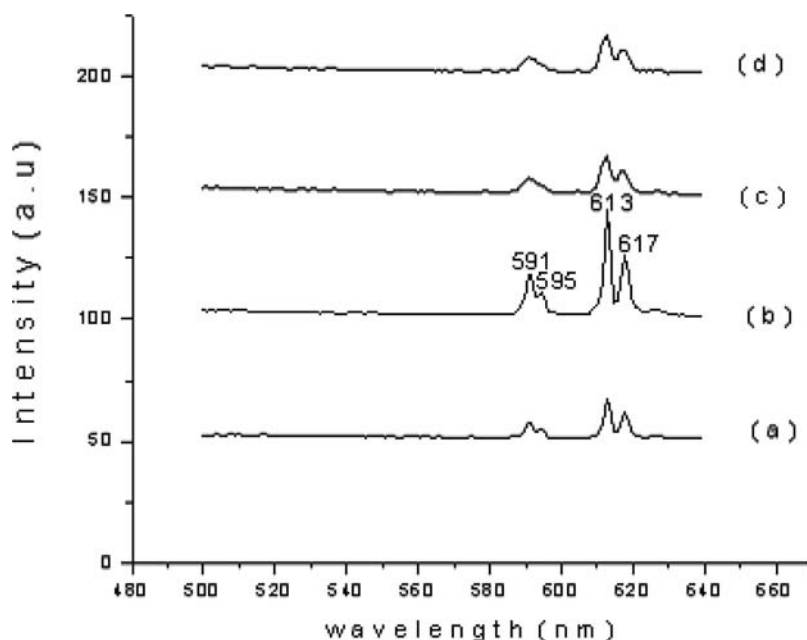


Figure 4 The emission spectra of $\text{YAL}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors doped with (a) 1 mol%, (b) 3 mol%, (c) 4 mol%, and (d) 5 mol% Eu^{3+} ions.

4. Conclusion

$\text{YAL}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors were prepared using the sol-gel method and calcined at 900°C for 4 hr. The XRD patterns are accordance with the standard XRD card of $\text{YAL}_3(\text{BO}_3)_4$ compound. The dopant Eu^{3+} replaces the Y^{3+} ion in $\text{YAL}_3(\text{BO}_3)_4$. Y atoms are surrounded by eight oxygen atoms in an arrangement which can be described as a trigonal bicapped antiprism, where Y^{3+} ion is in the centrosymmetric sites. As a new host lattice for Eu^{3+} activator for PDP applications, $\text{YAL}_3(\text{BO}_3)_4$ with trigonal space distorted R32 adopts the normal trigonal huntite type structure with Y-centered distorted trigonal prisms and Al-centered distorted octahedral dispersed between planes of BO_3 triangles that extend parallel to (001). In the excitation spectra, the adsorptions peaks at 416 nm, 466 nm, 523 nm result from the transitions of $^7\text{F}_1 \rightarrow ^5\text{D}_0$, $^7\text{F}_2 \rightarrow ^5\text{D}_0$, and $^7\text{F}_3 \rightarrow ^5\text{D}_0$, respectively. There are four emission peaks at 591, 595, 614, 613 and 617 nm, of which the emission peak at 613 nm is the strongest. The emission peaks at 591 and 595 nm result from the transition from $^5\text{D}_0 \rightarrow ^7\text{F}_1$, while the others at 613 and 617 nm are due to the transition from $^5\text{D}_0 \rightarrow ^7\text{F}_2$, induced by the lack of inversion symmetry at the Eu^{3+} site. The relative luminescent intensity of $\text{YAL}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors is largest when the doping concentration of Eu^{3+} ions is 3 mol%. These results show that the optimal doping concentration of Eu^{3+} ions in $\text{YAL}_3(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors is approximately 3 mol%.

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