Luminescence properties of $Y_{0.9-x}Gd_xEu_{0.1}Al_3(BO_3)_4$ $(0 \leqslant x \leqslant 0.9)$ phosphors prepared by spray pyrolysis process

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Abstract

Starting from metal nitrate aqueous solutions and H_3BO_3, $Y_{0.9-x}Gd_xEu_{0.1}Al_3(BO_3)_4$ $(0 \leqslant x \leqslant 0.9)$ phosphors were synthesized by spray pyrolysis followed by annealing at high temperature. The obtained phosphor particles have spherical morphology with size in the range 0.5–2 μm. Independent of the x values in $Y_{0.9-x}Gd_xEu_{0.1}Al_3(BO_3)_4$ $(0 \leqslant x \leqslant 0.9)$ phosphors, the Eu^{3+} ion shows its characteristic $^5D_{0,\,1}-^7F_J$ $(J = 0, 1, 2, 3, 4)$ transitions with $^5D_0-^7F_2$ red emission (612 nm) as the most prominent group. The photoluminescence intensity of phosphors increases with the increase of x value in $Y_{0.9-x}Gd_xEu_{0.1}Al_3(BO_3)_4$ $(0 \leqslant x \leqslant 0.9)$ due to an energy migration process like $Gd^{3+}-(Gd^{3+})_n-Eu^{3+}$ that occurred in the host materials.
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1. Introduction

The research on phosphors has a long history, and finding efficient luminescent materials is the researchers' long-term goal. Nowadays, much attention has been paid to improving the performance of the existing luminescent materials by controlling their morphology and microstructures. It was reported that phosphor particles with spherical morphology and the size of 1–3 μm could improve the optical performance due to the high packing density and the reduction of light scattering [1]. Spray pyrolysis (SP) is an effective method for preparing such materials. Phosphor particles prepared by this method have the characteristics of spherical shape, fine size, narrow size distribution and non-aggregation, all of which are for good optical performance in application [2–5].

Rare-earth borates are a useful class of hosts for luminescence due to their high VUV transparency and exceptional optical damage thresholds. For example, Eu^{3+}-doped (Y, Gd) BO_3 is a good phosphor currently

applied in plasma display panels (PDPs). However, this kind of phosphor suffers from poor color purity due to the emission $^5D_0-^7F_1$ (591 nm, red–orange color) as the most prominent group in the luminescence spectrum. So much attention has been paid for other borates for luminescence [6,7]. Among them the rare-earth aluminum borates $REAl_3(BO_3)_4$ (RE = rare-earth elements) are of special interest due to the pure red emission of Eu^{3+} (612 nm) in this kind of host lattices [6]. In this paper, we prepared the $Y_{0.9-x}Gd_xEu_{0.1}Al_3(BO_3)_4$ $(0 \leqslant x \leqslant 0.9)$ phosphors via SP process followed by annealing at high temperature, and investigated the dependence of the luminescent properties on the x values.

2. Experimental

The main starting materials for the synthesis of $Y_{0.9-x}Gd_xEu_{0.1}Al_3(BO_3)_4$ $(0 \leqslant x \leqslant 0.9)$ phosphors were rare-earth oxides Gd_2O_3, Y_2O_3 and Eu_2O_3 (all 99.99%, Shanghai Yuelong Non-Ferrous Metals Limited), $Al(NO_3)_3 \cdot 9H_2O$ (analytical reagent, A. R.) and H_3BO_3 (A. R.). The synthesis processes are as follows.

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Stoichiometric amounts of Y_2O_3, Gd_2O_3, and Eu_2O_3 were dissolved in dilute nitric acid under stirring and heating, and the excessive HNO_3 was driven off by further heating with final pH = 4–5. Then stoichiometric amount of $Al(NO_3)_3 \cdot 9H_2O$ and H_3BO_3 (30% excess) were dissolved in the above solution, and the resulting mixture was further stirred for 3 h. Then ammonia was dropped into the above solution until a colloidal solution formed. This solution was loaded to the SP apparatus (BüCHI Mini Spray Dryer B-191) to obtain SP precursor particles, which were annealed at 900 °C for 3 h in air to obtain the final products.

The post-annealed powder samples were checked by X-ray diffraction (Rigaku, D/max-II B) using Cu–Kα radiation ($\lambda = 0.15405$ nm). The morphology of the samples was inspected using scanning electron microscope (JEOL JXA-840). The excitation and emission spectra were taken on a Hitachi F-4500 spectrofluorimeter equipped with a 150 W xenon lamp as the excitation source. The luminescence decay curves were measured with a SPEX 1934D phosphorimeter using a 7 W pulsed xenon lamp as the excitation source with the pulse width of 3 µs. All the measurements were performed at room temperature.

3. Results and discussion

Fig. 1(a–c) shows the XRD patterns of $Y_{0.9-x}Gd_xEu_{0.1}Al_3(BO_3)_4$ ($x = 0$, 0.5, 0.9) phosphors, respectively. The standard XRD pattern for $YAl_3(BO_3)_4$ (JCPDS Card no. 15-0117) is also shown as a reference. It can be seen clearly that all the diffraction peaks of the synthesized $Y_{0.9-x}Gd_xEu_{0.1}Al_3(BO_3)_4$ ($x = 0$, 0.5, 0.9) phosphors are in good agreement with those of standard of $YAl_3(BO_3)_4$ (belonging to huntite structure with the space group R32, and hexagonal system with $a = 0.929$ nm, $c = 0.724$ nm) (JCPDS Card no. 15-0117), indicating that they possess the same crystal structure with $YAl_3(BO_3)_4$ independent of the x values. In other words, it can be said that the doped Eu^{3+}

ions have entered the host lattices of $Y_{0.9-x}Gd_xEu_{0.1}Al_3(BO_3)_4$ ($x = 0$, 0.5, 0.9) completely and do not change the crystal structure. All the diffraction peaks $Y_{0.9-x}Gd_xEu_{0.1}Al_3(BO_3)_4$ ($x = 0$, 0.5, 0.9) can be indexed according to those of $YAl_3(BO_3)_4$, as shown in Fig. 1(c). Furthermore, it is reasonably expected that a complete solid solution can be formed in $Y_{0.9-x}Gd_xEu_{0.1}Al_3(BO_3)_4$ ($0 \leqslant x \leqslant 0.9$) series phosphors due to the same crystal structure of $Y_{0.9}Eu_{0.1}Al_3(BO_3)_4$ and $Gd_{0.9}Eu_{0.1}Al_3(BO_3)_4$.

As a representative example, the SEM micrograph of $Gd_{0.9}Eu_{0.1}Al_3(BO_3)_4$ phosphor is shown in Fig. 2. It can be seen that the phosphor possesses spherical morphology with size ranging from 0.5 to 2 µm. This is the characteristics of the phosphors prepared by the SP process, and the spherical morphology is good to improve the comprehensive performance of the phosphor materials for practical application [2–5].

Figs. 3(a) and (b) shows the excitation and emission spectra of $Gd_{0.9}Eu_{0.1}Al_3(BO_3)_4$ phosphor, respectively. The excitation spectrum contains an intense broad band with a maximum at 256 nm and a group of lines in the longer wavelength region. The former is due to the charge transfer band (CTB) of Eu^{3+}–O^{2-}, and the latter excitation peaks at 277 nm (^8S–^6I) and 310 and 315 nm (^8S–^6P) originate from Gd^{3+} in the host lattices, and other excitation peaks (322 nm: $^7F_0$–$^5H_6$, 365 nm: $^7F_0$–$^5D_4$, 385 nm: $^7F_0$–$^5G_2$, 397 nm: $^7F_0$–$^5L_6$, 417 nm: $^7F_0$–$^5D_3$, 468 nm: $^7F_0$–$^5D_2$) arise from the f–f transitions within Eu^{3+} $4f^6$ configuration. Excitation into the CTB of Eu^{3+} at 256 nm (or Gd^{3+} at 277 nm) yields the emission spectrum as shown in Fig. 3(b), which is composed of $^5D_{0,1}$–^7F_J ($J = 1, 2, 3, 4$, as labeled in the figure) emission lines of Eu^{3+} dominated by the $^5D_0$–$^7F_2$ (612 nm) forced electric-dipole transition. This indicates that the Eu^{3+} ions are located at sites without inversion symmetry in the host lattices [8]. The spectrum also shows many additional lines due to the splitting of ^7F_J ($J = 0$–6) ground states by the crystal field. The $^5D_0$–$^7F_1$ and $^5D_0$–$^7F_2$ transitions consist of two and three separate
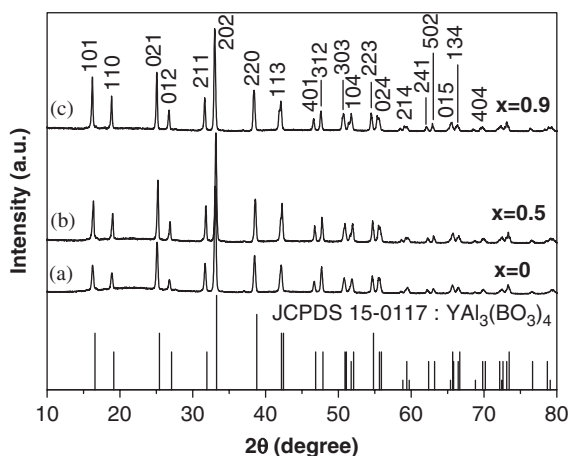

Fig. 1. XRD patterns for $Y_{0.9-x}Gd_xEu_{0.1}Al_3(BO_3)_4$ ($x = 0$, 0.5, 0.9) by SP process and the standard $YAl_3(BO_3)_4$ (JCPDS card 15-0117) as a reference.
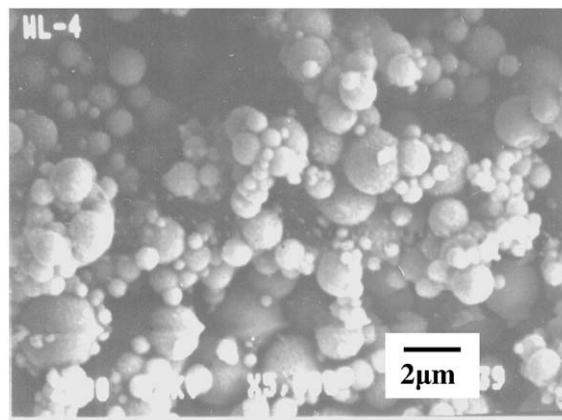

Fig. 2. SEM micrograph of $Gd_{0.9}Eu_{0.1}Al_3(BO_3)_4$ phosphor by SP process followed by annealing at 900 °C.