Synthesis and Luminescence Properties of (Y, Gd) (P, V)O₄:Eu³⁺, Bi³⁺Red Nano-phosphors with Enhanced Photoluminescence by Bi³⁺, Gd³⁺ Doping

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(Received 16 Jan 2013; accepted 13 May 2013; published online 26 May 2013.)

Abstract: A series of (Y₁₋₇, Gd₇)₀.₉₅₋ₓ(P₇, V₁₋₇)O₄:0.₀₅Eu³⁺, xBi³⁺ phosphors have been successfully prepared by a subsection method. The crystal structure, surface morphology and luminescence properties were investigated. It was found that the sintered samples crystallized in a tetragonal crystal system with space group I₄₁/amd (a = b = 0.₇₁₁₉ nm, c = 0.₆₂₉₀ nm). The products presented rod-like morphology with length of 100-150 nm and width of 50-100 nm. A maximum peak at 619 nm (⁵D₀ → ⁷F₂) was observed in emission spectrum of the phosphors. It was also found that co-doping of Bi³⁺, P⁵⁺ and Gd³⁺ ions into YVO₄:Eu³⁺ can not only made the right edge of the excitation band shift to the long-wavelength region, but also increased the emission intensity at 619 nm sharply and decreased the lifetime of fluorescence decay. These results may expand the application scope of the phosphors.

Keywords: (Y, Gd)(P, V)O₄:Eu³⁺,Bi³⁺; Rod-like; Red phosphors; Photoluminescence; Doping


Introduction

Over past decades, many efforts have been made to study the rare-earth doped luminescence materials, which have been largely applied in fields of illuminations and displays, such as fluorescent lamps, cathode-ray tubes, field emission displays, plasma display panels, electro-optical polarizers and white light-emitting diodes [1-7]. Yttrium vanadate (YVO₄) has been proved one of the best candidates for doping into rare earth ions [8] since it provides a suitable Y³⁺ site where trivalent rare-earth ions can be replaced without additional charge compensation. In particular, as a typical red-emitting phosphor, europium doped YVO₄ has been explored in many fields [8-11]. Recent years, much attention has been focused on the nanoscale phosphors. It was found that the higher packing density and better paste rheology of smaller-sized phosphors particles led to higher screen resolution and lower screen load [12-16]. Especially, Eu³⁺ doped nanoscaled YVO₄ phosphor has attracted a great deal of attention. Nowadays, a number of methods, such as single crystal growth techniques, the solution combustion process, hydrolyzed colloid reaction (HCR), solution-based sol-gel process and hydrothermal reaction have been used to synthesize the YVO₄:Eu³⁺ nanophosphors. However, due to lower crystallinity and higher surface defect density, most products have lower luminescent intensity compared with their bulk powders. For exam-

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ple, compared with commercial PDP red phosphor (Y, Gd)BO$_3$:Eu$^{3+}$, YVO$_4$:Eu$^{3+}$ nanoparticles have higher color purity but lower luminescent intensity, especially when the particle size decreased into nanosized scale [15].

Many efforts have been made to improve luminescence properties of YVO$_4$:Eu$^{3+}$ nanophosphors [17-21]. For example, sensitizer co-doping has been proved to be an efficient way to increase the luminescence efficiency. Till now, many researches are focused on one kind of ions doped into YVO$_4$:Eu$^{3+}$ nanophosphors. It is relatively less reports on multi-ions co-doping. It was found that high concentration doping of Gd$^{3+}$ and P$^{5+}$ into YVO$_4$:Eu$^{3+}$ would increase the photoluminescence intensity [3,19]. And Bi$^{3+}$ ion can be used as a sensitizer to strengthen and broaden the ultraviolet-vacuum ultraviolet (UV-VUV) excitation bands [10]. In this paper, three kinds of ions (Bi$^{3+}$, P$^{5+}$ and Gd$^{3+}$) were co-doped into YVO$_4$:Eu$^{3+}$ to improve the photoluminescence properties by using a subsection method.

Experimental

Materials and reagents

The materials and reagents used in the experiment were Y$_2$O$_3$ (99.99% purity), Gd$_2$O$_3$ (99.99% purity), Eu$_2$O$_3$ (99.99% purity), Bi(NO$_3$)$_3$·5H$_2$O (A.R.), NH$_4$VO$_3$ (A.R.), (NH$_4$)$_2$HPO$_4$ (A.R.), HNO$_3$ (A.R.), Polyethylene glycol (PEG, molecular weight = 20000, A.R.), Anhydrous ethanol (A.R.), NH$_3$·H$_2$O (A.R.), Citric acid (A.R.) and enough distilled water.

Synthesis of (Y, Gd)(P, V)O$_4$:Eu$^{3+}$, Bi$^{3+}$ samples

All samples were prepared by a two-step subsection method. The YVO$_4$:Eu$^{3+}$, Bi$^{3+}$ crystal seeds were prepared by a solvothermal method and Gd$^{3+}$, P$^{5+}$ were doped into YVO$_4$:Eu$^{3+}$, Bi$^{3+}$ by a sol-gel process. In a typical solvothermal synthesis process, the YVO$_4$:Eu$^{3+}$ crystal seeds were dissolved in excess diluted nitric acid to form a mixture. Then, proper quantity of Bi(NO$_3$)$_3$·5H$_2$O and NH$_4$VO$_3$ (molar ratio of Y:Eu:Bi:V = 0.90:0.05:0.05:1), 50 ml anhydrous ethanol and distilled water (E:W = 1:1) were mixed and added into the above mixture under ultrasonic mixing for 0.5 h to form a total solution. The initial pH value of the solution was adjusted to 7 using NH$_3$·H$_2$O. After that, the solution was transferred into a 100 ml stainless steel Teflon-lined autoclave and heated at 200℃ for 12 h. After filtered and washed with distilled water by ethanol several times, the product was dried and white YVO$_4$:Eu$^{3+}$ nanoparticles was obtained.

In the sol-gel process, proper quantity of Gd$_2$O$_3$, Eu$_2$O$_3$ and (NH$_4$)$_2$HPO$_4$ (Gd:Eu:P = 0.95:0.05:1) were dissolved in excess diluted nitric acid and evaporated to dryness. The mixture was then dissolved in a 50 ml mixed solution of anhydrous ethanol and distilled water (E:W = 1:1). Proper quantity of citric acid was added as a chelating agent for the metal ions under magnetic stirring (the molar ratio of metal ions to citric acid was 1:2). The proper quantity of polyethylene glycol (molecular weight = 10000, A.R.) was added as a cross-linking agent. Afterwards, a certain quantity of YVO$_4$:Eu$^{3+}$ nanoparticles, which obtained in the solvothermal method process, were added under stirring. The pH value of the solution was adjusted to 2 by using NH$_3$·H$_2$O and the solution was stirred at 60℃ for 1 h to form a gel. The gel was dried in an oven at 100℃ and ground in an agate mortar for 10-30 min. The porous dried gel was then sintered at 1000℃ for 2 h.

Characterization

The structure of the products was analyzed by using a SHIMADZU polycrystalline XRD (Xpert PRD MPD) with Cu-Kα radiation (40 kV, 40 mA, Kα = 0.15418 nm). The surface morphology was observed by a JEOL-JSM5900 and a Quanta 450 scanning electron microscopy (SEM). The excitation spectra, emission spectra and decay curves were recorded on a HITACHI F-7000 fluorescence spectrophotometer. All the measurements were done at room temperature.

Results and discussion

Figure 1 shows the collected XRD patterns of (a) Y$_{0.95}$VO$_4$:0.05Eu$^{3+}$ crystal seeds, (b) Y$_{0.9}$VO$_4$:0.05Eu$^{3+}$,0.05Bi$^{3+}$ crystal seeds, (c) the precursor prepared in the sol-gel process and (d) the final products (Y$_{0.5}$, Gd$_{0.5}$)$_{0.9}$(P$_{0.5}$, V$_{0.5}$)O$_4$:0.05Eu$^{3+}$,0.05Bi$^{3+}$ crystals sintered at 1000℃ for 2 h. In order to explore the phase structure, the diffraction peaks of the samples are indexed on the basis of the single crystal YVO$_4$ (JCPDS No. 17-0341) in a tetragonal crystal system with space group I4$_1$/amd and GdPO$_4$ (JCPDS No. 32-0386) in a monoclinic system with space group P2$_1$/n. All XRD peaks in Fig. 1(a) are in good agreement with the values of standard YVO$_4$ (JCPDS No. 17-0341). Since Eu$^{3+}$ and Y$^{3+}$ ions have the same valence and similar atomic radius, the doped Eu$^{3+}$ has little effect on the structure of YVO$_4$. Compared with Fig. 1(a), Fig. 1(b) indicates a pure phase of Y$_{0.9}$VO$_4$:0.05Eu$^{3+}$,0.05Bi$^{3+}$ without obvious impurities. It can be also observed that Bi$^{3+}$ doping will strengthen the peak intensity. In Fig. 1(c),
a mixture containing YVO₄ and GdPO₄ was found. However, the peaks for GdPO₄ phase were not observed in final product (see Fig. 1(d)). The samples still keep a tetragonal phase with space group I₄₁/amd \((a = b = 0.7119\text{ nm}, c = 0.6290\text{ nm})\), which indicates Gd³⁺ and P⁵⁺ were doped in the sample after sintered at 1000°C for 2 h. In addition, a systematic shifting of diffraction angle \(2\theta\) towards larger angle directions was observed, which is due to the different radius of the host ions and the doping ions. Since the radius difference between V⁵⁺ and P⁵⁺ is bigger than that between Y³⁺ and Gd³⁺, the cell volumes decreased with increasing the same content rates of Gd³⁺ (Eu³⁺, Bi³⁺) and P⁵⁺. As a result, the diffraction peaks shifted to the larger angle gradually.

Figure 2 shows SEM images of several representative samples. One can see that the merchant phosphors in Fig. 2(a) are composed of large grains with average size about 1 μm. However, the seeds shown in Fig. 2(b) have spherical or approximately spherical morphology with about 50 nm in size, and the as-prepared particles (see Fig. 2(c),(d)) are short rod-like with average size about 100 nm length and 50 nm width. From Fig. 2(c,d), it was also found that the particles obtained by the solvothermal method are more uniform than those by the hydrothermal method. Figure 3 shows SEM images of \(Y_{1-x}Gd_x\)(Pₓ,V₁₋ₓ)O₄:0.05Eu³⁺, 0.05Bi³⁺ with different doping content. One can see that the particle sizes increase gradually with the quantity of Gd³⁺ and P⁵⁺ doping. When doping quantity \(x\) is 0.5, the
particles present normal rod-like morphology and the particle size increases obviously. When doping quantity $x$ is up to 0.75, the sample consists of irregular particles. These results indicate that co-doping Gd$^{3+}$ and P$^{5+}$ will increase the particle size and change the particle morphology obviously. This can be understood that YVO$_4$ particles prepared by the solvothermal method played a role as template to control the shape of the final products due to the template-induced effect of the seed. During the calcine processes, the P$^{5+}$ and Gd$^{3+}$ ions were diffused into the YVO$_4$ particles readily. It will weaken the limit effect of the seeds through increase the concentration of P$^{5+}$ and Gd$^{3+}$ ions continuously so that the phosphor particles approach to natural growth. Moreover, the rare earth orthophosphates generally have hexagonal or tetragonal structure and tend to form a wire-like or rod-like morphology [22].

Figure 4 shows the excitation spectra of (a) Y$_{0.95}$VO$_4$: 0.05Eu$^{3+}$, (b) Y$_{0.9}$VO$_4$: 0.05Eu$^{3+}$, 0.05Bi$^{3+}$, (c) Y$_{0.9}$ (P$_{0.5}$, V$_{0.5}$)O$_4$: 0.05Eu$^{3+}$, 0.05Bi$^{3+}$ and (d) (Y$_{0.5}$, Gd$_{0.5}$)$_{0.9}$(P$_{0.5}$, V$_{0.5}$)$_{0.1}$O$_4$: 0.05Eu$^{3+}$, 0.05Bi$^{3+}$ phosphors. The excitation spectra were measured in the range of 200-500 nm by monitoring the emission of Eu$^{3+}$ at 619 nm ($^5D_{0} \rightarrow ^7F_2$). As shown in Fig. 4(a), the excitation spectrum of Y$_{0.95}$VO$_4$: 0.05Eu$^{3+}$ consists of a broad band (210-350 nm) which is owing to the overlap of two peaked at about 275 and 325 nm. The short-wavelength excitation is due to the charge-transfer processes involving the Y-O components, while the long-wavelength excitation is due to the V-O components of the matrix [15]. When Bi$^{3+}$ is doped into Y$_{0.95}$VO$_4$: 0.05Eu$^{3+}$ particles, the intensity of the charge transfer (CT) bands (Eu-O and V-O interactions) increased and the right edge of the band shifted to near 400 nm (Fig. 4(b)), which ascribed to the intense absorption of Bi$^{3+}$ compounds in the band of 250-400 nm. Related reports show that the absorption energy of Bi$^{3+}$ could transfer to Eu$^{3+}$, which can

![Fig. 3 SEM images of (Y$_{1-x}$, Gd$_x$)$_{0.9}$ (P$_x$, V$_{1-x}$) O$_4$:0.05Eu$^{3+}$, 0.05Bi$^{3+}$ crystals with (a) $x = 0$; (b) $x = 0.25$; (c) $x = 0.5$; (d) $x = 0.75$.](image)

![Fig. 4 The excitation spectra of (a) Y$_{0.95}$VO$_4$: 0.05Eu$^{3+}$; (b) Y$_{0.9}$VO$_4$: 0.05Eu$^{3+}$, 0.05Bi$^{3+}$; (c) Y$_{0.9}$ (P$_{0.5}$, V$_{0.5}$) O$_4$: 0.05Eu$^{3+}$, 0.05Bi$^{3+}$ and (d) (Y$_{0.5}$, Gd$_{0.5}$)$_{0.9}$(P$_{0.5}$, V$_{0.5}$)$_{0.1}$O$_4$: 0.05Eu$^{3+}$, 0.05Bi$^{3+}$ phosphors ($\lambda_{em} = 619$ nm).](image)
sensitize and enhance the intensity of Eu$^{3+}$ [18]. When P$^{5+}$ is doped into the Y$_{0.9}$VO$_4$:0.05Eu$^{3+}$,0.05Bi$^{3+}$ particles, the intensity of the excitation spectra will increase (Fig. 4(c)), especially the intensity of the band 320 nm-375 nm will enhance obviously. It may be resulted that doping of P$^{5+}$ can enhance the CT band of Bi$^{3+}$→O$^{2-}$ efficiently [19]. Furthermore, the intensity of the excitation spectra increased when Gd$^{3+}$ is doped into the sample (Fig. 4(d)). This is because co-doping Gd$^{3+}$ can produce more efficient excitation of Eu$^{3+}$ in UV region [15].

Figure 5(a) shows emission spectra of Y$_{0.95}$VO$_4$:0.05Eu$^{3+}$; Y$_{0.9}$VO$_4$:0.05Eu$^{3+}$, 0.05Bi$^{3+}$; Y$_{0.9}$(P$_{0.5}$, V$_{0.5}$)$_4$:0.05Eu$^{3+}$, 0.05Bi$^{3+}$ and (Y$_{0.5}$, Gd$_{0.5}$)$_4$:0.05Eu$^{3+}$,0.05Bi$^{3+}$, 0.05Eu$^{3+}$,0.05Bi$^{3+}$ phosphors. For all the phosphors, two typical emission peaks of Eu$^{3+}$ activators are located mainly in the red region (594 nm and 619 nm), which is due to the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions when excited under 275 nm. The emission peak near 700 nm is associated with the $^5D_0 \rightarrow ^7F_4$ transition. The strongest emission peak is at 619 nm indicating the final products have fine color purity. It can be obviously seen from Fig. 5(a) that the emission intensity at 619 nm under 275 nm excitation increased after Bi$^{3+}$ doping into YVO$_4$:Eu$^{3+}$. It is also obvious that co-doping of P$^{5+}$ and Gd$^{3+}$ can enhance the emission intensity. This is because the incorporation of P$^{5+}$ and Gd$^{3+}$ into the YVO$_4$:Eu$^{3+}$, Bi$^{3+}$ lattice will increase the absorption of excitation energy and produce more efficient excitation of Eu$^{3+}$, thus enhancing the PL characteristics. The emission spectrum of Y$_{0.9}$VO$_4$:0.05Eu$^{3+}$, 0.05Bi$^{3+}$ excited under 365 nm is shown in the inset of Fig. 5(a). One can find that the emission intensity of $^5D_0 \rightarrow ^7F_2$ electric dipole transition of Eu$^{3+}$ at 619 nm under 365 nm excitation, which has about two-thirds intensity of that under 275 nm excitation, increases sharply with the doping of Bi$^{3+}$ ions. It indicates that Bi$^{3+}$ doping can obviously enhance the emission intensity at 619 nm when excited under 365 nm. Figure 5(b) shows the influence of Bi$^{3+}$ concentration on the relative emission intensity of (Y$_{0.5}$, Gd$_{0.5}$)$_{0.9}$→(P$_{0.5}$, V$_{0.5}$)$_4$:0.05Eu$^{3+}$,xBi$^{3+}$ at 619 nm under 275 nm excitation. The curve shows that with increase of Bi$^{3+}$ concentration, the emission intensity increased. As Bi$^{3+}$ concentration is more than 5 mol%, the luminous intensity decreases gradually. The sensitization of Bi$^{3+}$ to Eu$^{3+}$ depends on the concentration of Bi$^{3+}$, and the most suitable concentration of Bi$^{3+}$ is 5 mol%.

Figure 6 shows a comparison of the room-temperature luminescence decay curves of the $^5D_0 \rightarrow ^7F_2$ transition of Eu$^{3+}$ between Y$_{0.95}$ (P$_{0.5}$, V$_{0.5}$)$_4$:0.05Eu$^{3+}$, (Y$_{0.5}$, Gd$_{0.5}$)$_{0.9}$→(P$_{0.5}$, V$_{0.5}$)$_4$:0.05Eu$^{3+}$ and (Y$_{0.5}$, Gd$_{0.5}$)$_{0}$→(P$_{0.5}$, V$_{0.5}$)$_4$: 0.05Eu$^{3+}$, 0.05Bi$^{3+}$ under 275 nm excitation. The decay kinetics behavior depends on the number of different luminescent centers, defects, energy transfer and impurities in the host [23]. It is possible to explore the influence of co-doped elements on the decay dynamics of the samples. It can be clearly seen that, the emission of the $^5D_0 \rightarrow ^7F_2$ transition of Eu$^{3+}$ decays exponentially, which can be well-fitted into the following exponential function:

\[ I(t) = I_0 \exp(-t/\tau) + C \]

where $I(t)$ and $I_0$ is the luminescence intensity at time $t$ and initial time, $C$ is a constant which relates to the test equipment, $t$ is the time and $\tau$ is the decay lifetime for the exponential components, respectively. The measurement results of the luminescence lifetime...
of the as-synthesized $Y_{0.95}(P_{0.5},V_{0.5})O_4$:0.05Eu$^{3+}$, $(Y_{0.5},Gd_{0.5})_{0.95}(P_{0.5},V_{0.5})O_4$:0.05Eu$^{3+}$ and $(Y_{0.5},Gd_{0.5})_{0.9}(P_{0.5},V_{0.5})O_4$:0.05Eu$^{3+}$, 0.05Bi$^{3+}$ samples at 619 nm emission under 275 nm excitation are 862.59, 805.12 and 525.38 μs, respectively. Due to the excitation energy transfer occurs in a very short time in comparison with the relatively long fluorescence decay time, the nature of non-exponential decay cannot be attributed to the excitation energy transfer [25]. It can be noticed that with the doping of Bi$^{3+}$, the luminescence lifetime of $(Y_{0.5},Gd_{0.5})_{0.9}(P_{0.5},V_{0.5})O_4$:0.05Eu$^{3+}$, 0.05Bi$^{3+}$ upon 275 nm decreased a lot. This phenomenon indicates that Bi$^{3+}$ can involve the energy transfer rate among Eu$^{3+}$ and other ions, correlated to the decay lifetime. Therefore, further researches on the formation of the energy transfer after the introduction of Bi$^{3+}$ and other ions into Y(P, V)O$_4$:Eu$^{3+}$ become very important.

Conclusions

In this paper, series of $(Y_{1-y},Gd_y)_{0.95-x}(P_y,V_{1-y})O_4$:0.05Eu$^{3+}$, xBi$^{3+}$ samples have been synthesized successfully through a subsection method. When doping concentration were $x = 0.05$, $y = 0.5$, the samples showed pure phase and present rod-like morphology. The morphology and size of the samples could be controlled by adjusting the ratios between the seeds and the doping ions. The average sizes for the phosphor particles were 100-150 nm length and 50-100 nm width. With the doping of Bi$^{3+}$, P$^{5+}$ and Gd$^{3+}$ ions, the samples showed high red emission at 619 nm ($^5D_0 \rightarrow ^7F_2$), superior color saturation and broad excitation band (210-400 nm). The doping of Bi$^{3+}$ and Gd$^{3+}$ can increase the emission intensity at 619 nm under 365 nm excitation, and Bi$^{3+}$ could decrease the fluorescent lifetime. The advantages may expand the application of the samples.

Acknowledgements

The authors would like to thank Chongqing Key Laboratory of Micro/Nano Materials Engineering and Technology. This work was supported by the Program for New Material Development & Application innovation Research Team of Higher Education in ChongQing of China (Grant No. 201042).

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