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A novel Dy^{3+}-doped $GdPO_4$ white-light phosphors under vacuum ultraviolet excitation for Hg-free lamps application*

Han Guo-Cai(韩国才)[a)], Wang Yu-Hua(王育华)[a)b)†],
Wu Chun-Fang(吴春芳)[a)b)], and Zhang Jia-Chi(张加驰)[a)]

[a)] *Department of Material Science, School of Physical Science and Technology, Lanzhou University, Lanzhou* 730000, *China*
[b)] *Key Laboratory for Magnetism and Magnetic Materials of the Ministry of Education, Lanzhou University, Lanzhou* 730000, *China*

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Novel Dy^{3+}-doped $GdPO_4$ white light phosphors with monoclinic system were successfully synthesised by hydrothermal method at 240 °C. This paper investigates the luminescence properties of white-light $Gd_{1-x}PO_4 : xDy^{3+}$ under vacuum ultraviolet (VUV) excitation. The strong absorption at around 147 nm in excitation spectrum energy can be transferred to the energy levels of Dy^{3+} ion from the host absorption. Additionally, this white light phosphors are activated by a single Dy^{3+} ion and with a lower preparation temperature, which tend to decrease the consumption of rare earth resource and energy. Therefore, the luminescence of $Gd_{1-x}PO_4 : xDy^{3+}$ under VUV excitation is effective, and proves to be promising in application to mercury-free lamp.

Keywords: vacuum ultraviolet, hydrothermal synthesis, phosphors
PACC: 7855, 7860

1. Introduction

Recently, luminescence materials doped with Dy^{3+} have drawn much attention for its white emission.[1−4] In general, Dy^{3+} has two dominant bands in the emission spectra in many host matrixes. The band located at 572 nm (yellow) corresponds to the hypersensitive transition $^4F_{9/2}{}^-{}^6H_{13/2}(\Delta L = 2, \Delta J = 2)$, and another one located at 478 nm (blue) corresponds to the transition $^4F_{9/2}{}^-{}^6H_{15/2}$. By adjusting the yellow-to-blue intensity ratio (Y/B) value appropriately, it is possible to obtain near-white emission with only Dy^{3+}-actived luminescence materials. Therefore Dy^{3+}-activated phosphors are promising white light phosphors and can be used in mercury-free lamp. For a mercury-free lamp, the excitation energy was mainly composed of vacuum ultraviolet (VUV) radiation but most of VUV energy is absorbed by the host crystal, if the energy can be transferred from host to rare-earth (RE) ions, the RE ions can emit visible light. So the host absorption efficiency and the energy transfer efficiency are very important part in VUV-excited phosphors being applied to a mercury-free lamp.

The RE-ions-doped phosphate-based phosphors have been applied in various fields, such as plasma display panels, a mercury-free lamp and visible lasers.[1−5] $LnPO_4 : Tb, Bi(Ln = La, Gd)$ phosphors[5] shows the strong emission intensity in VUV region. In $GdPO_4 : Eu$[6] the high absorption of PO_4^{3+} was observed in VUV region. Also, Jüstel *et al*[7] pointed out that phosphate is an efficient host under VUV excitation. According to the results of energy levels calculated by the extended Hückel method[8] on PO_4^{3-}, and diffuse reflection spectra measurement of RPO_4 (R = Y, La, Gd, and Lu),[9] it can be concluded that orthophosphates are promising host materials for its application in VUV region.

However, up to now, the photoluminescence properties in VUV range of Dy^{3+} doped RE phosphate prepared by hydrothermal method has scarcely been reported. So in this work, we synthesis'ed Dy^{3+}-doped $GdPO_4$ phosphors by the hydrothermal method. Meanwhile, photoluminescence properties of

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†Corresponding author. E-mail: wyh@lzu.edu.cn

Dy^{3+}-doped $GdPO_4$ phosphors in VUV region were also investigated.

2. Experimental procedure

Preparation of $Gd_{1-x}PO_4 : xDy^{3+}$ by hydrothermal method is as follows: first, The purities of $(NH_4)_2HPO_4$ is AR, and that of Gd_2O_3 and Dy_2O_3 are better than 99.99%. The doping amount x of Dy_2O_3 is from 0.02% to 0.10%. Appropriate amounts of high purity of Gd_2O_3 and Dy_2O_3 were dissolved into concentrated HNO_3 (65%), and then appropriate volume of distilled water was added. An appropriate volume of $(NH_4)_2HPO_4$ aqueous solution was then added to the solution. The final pH value was adjusted to 2 with aqueous ammonia (NH_4OH) solution. Then the mixture is transferred into a Teflon-lined stainless steel autoclave with a filling capacity of 40%, hydrothermal reaction lasts 6 h at 240 °C and cooled to room temperate. The obtained suspension was filtered repeatedly and then dried in an oven at 90 °C in air.

The power x-ray diffraction (XRD) patterns of samples was carefully collected in the 2θ range 10°–80° by powder XRD (Rigaku D/MAX-2400 x-ray diffractometer with Ni-filtered Cu Kα radiation).

The excitation and emission spectra were measured by using an Edinburgh Instruments FLS920T. The scan speed was 30 nm/m with a step of 1 nm and the dwell time was 0.2 s. The VUV light source of the spectrometer system was a 150-W deuterium lamp (Cathodeon Incorporated). The emission and excitation spectra were measured by the vacuum monochromator (VM504, Acton Research Corporation, ARC). The slits for the excitation and the emission spectra were 0.18 nm and 6 nm, respectively. The VUV excitation spectrum was corrected by dividing the excitation intensity of sodium salicylate.

3. Results and discussion

The XRD pattern of the typical sample $Gd_{1-x}PO_4 : xDy^{3+}$ was shown in Fig.1, indexed by monoclinic structure and was proved to be single phase based on the JCPDS card 32-0386. The XRD patterns of other samples were also similar.

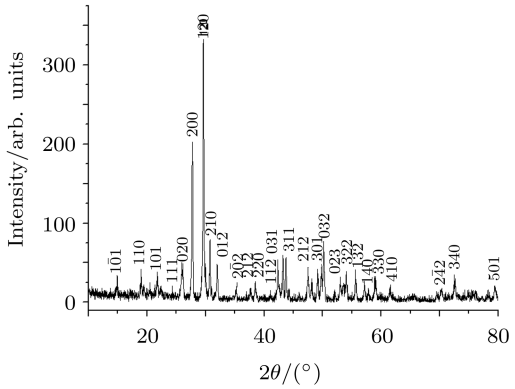


Fig.1. The powder XRD pattern of $GdPO_4 : Dy^3$.

Figure 2 shows emission spectrum of $Gd_{1-x}PO_4 : xDy^{3+}$ under 147 nm excitation. From Fig.2, the peaks at 312 nm, 404 nm, 460 nm, 478 nm, 572 nm and 660 nm could be attributed to $^6P_{7/2}$–$^8S_{17/2}$, $^4F_{7/2}$–$^6H_{15/2}$, $^4F_{7/2}$–$^6H_{13/2}$, $^4F_{9/2}$–$^6H_{15/2}$, $^4F_{9/2}$–$^6H_{13/2}$, $^4F_{9/2}$–$^6H_{11/2}$ transitions of Dy^{3+}, respectively. These attributions are similar to the other systems in Refs.[10] and [11]. The $^4F_{9/2}$–$^6H_{15/2}$ transition is mainly magnetically allowed and hardly varies with the environment, while $^4F_{9/2}$–$^6H_{13/2}$ transition (yellow) belongs to hypersensitive transition and is strongly influenced by outside surroundings.[12] The relative intensity of them depends strongly on the local symmetry of Dy^{3+}, and a lower symmetry local site will result in a higher ratio of the yellow to the blue as shown in Ref.[13]. From our result, the ratio of yellow to blue was larger than 1, indicating the site Dy^{3+} is located with lower symmetry. In the samples, it is obvious that the intensities of the peaks at 478 nm and 572 nm are gradually enhanced along with increase in x and become dominant when $x = 0.08$, then decrease when $x > 0.08$. Therefore, by

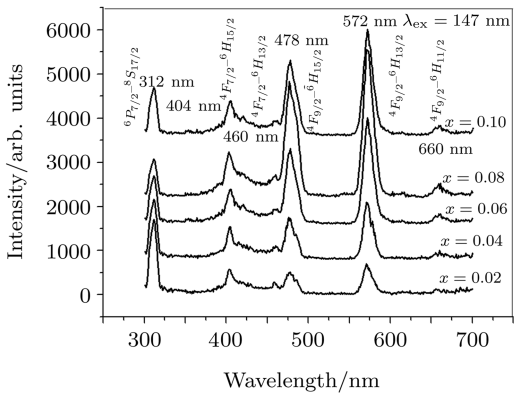


Fig.2. The emission spectra of $Gd_{1-x}PO_4 : xDy^{3+}$ ($0.02 \leq x \leq 0.10$).

adjusting the yellow-to-blue intensity ratio (Y/B) value, the chromaticity coordinates in white light zone of $Gd_{1-x}PO_4:xDy^{3+}$ phosphors can be obtained.

Figure 3 shows the influence for luminescence intensity of the main emission peaks at 572 nm, along with the increase in doping concentration x of $Gd_{1-x}PO_4:xDy^{3+}$. From Fig.3, it is clear that the luminescence intensity of $Gd_{1-x}PO_4:xDy^{3+}$ increases along with increase in x, when $x = 0.08$, the luminescence intensity is the strongest.

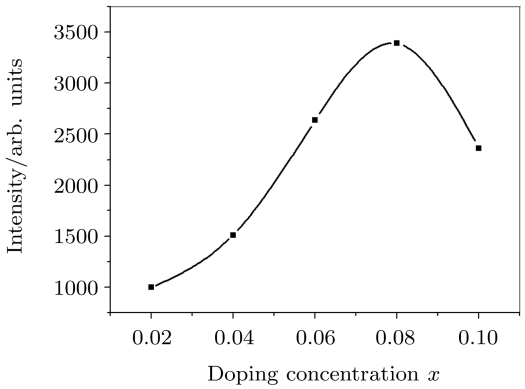


Fig.3. The influence for luminescence intensity of the main emission peaks at 572 nm along with the increase in doping amount x.

Figure 4 shows the excitation spectrum of $Gd_{0.92}PO_4:0.08Dy^{3+}$ monitored at 572 nm. In the excitation spectrum, the broad band ranging from 125 nm to 165 nm could be attributed to the host absorption of phosphate, and the similar observations in other system have been also attributed in Refs.[14] and [15]. The band at around 182 nm should be attributed to f–d transition of Dy^{3+}. We can predict the position of Dy^{3+} f–d transition with the following P. Dorenbos expression[16,17]

$$E(\mathrm{Ln,A}) = 49340D(\mathrm{A}) + \Delta E^{\mathrm{Ln,Ce}}(\mathrm{cm}^{-1}), \quad (1)$$

where E(Ln,A) is the f–d energy difference in unit of cm^{-1} of lanthanide ion Ln^{3+} doped in compound A with the so-called crystal field depression D(A). The 49340 cm^{-1} is the energy of the first f–d transition of Ce^{3+} as a free (gaseous) ion. The $\Delta E^{\mathrm{Ln,Ce}}$ is defined as the difference in f–d energy of Ln^{3+} with that of the first electric dipole allowed transition in Ce^{3+}. In Ref.[17], D(A) is 16007 cm^{-1} ($GdPO_4$) , and $\Delta E^{\mathrm{Ln,Ce}}$ is 25100±610 cm^{-1}. Therefore, by Eq.(1), we can calculate the f–d transition position of Dy^{3+} in the system as 171±2 nm, which is close to those shown in Fig.4.[18,19]

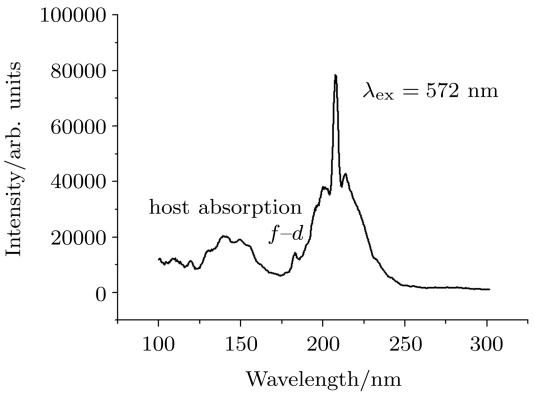


Fig.4. The excitation spectrum of $Gd_{0.92}PO_4:0.08Dy^{3+}$.

Figure 5 shows the chromaticity coordination (x, y) of $Gd_{1-x}PO_4:xDy^{3+}$ excited under 147 nm in the CIE 1931 chromaticity diagram. It is obvious that the chromaticity coordinates of $Gd_{1-x}PO_4:xDy^{3+}$ gradually moves to the warm white side and approaches the yellow region along with decrease in x; when $x > 0.08$, it moves to the cold white side in contrary orientation which could arise from the ratio of luminescence intensity of the peaks located at 478 nm and 572 nm. Detailed chromaticity coordinates are shown in Table 1, which are located in white light region.

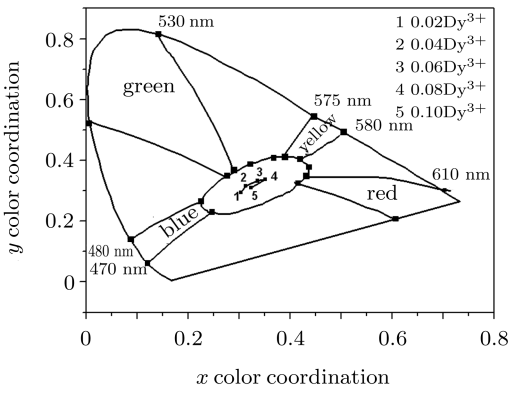


Fig.5. The chromaticity coordinates (x, y) of $Gd_{1-x}PO_4:xDy^{3+}$ under 147 nm excitation in the CIE 1931 chromaticity diagram.

Table 1. The chromaticity coordination of $Gd_{1-x}PO_4:xDy^{3+}$ $(0.02 \le x \le 0.10)$.

the amount of doping x	the chromaticity coordination x	the chromaticity coordination y
$x = 0.02$	0.298	0.294
$x = 0.04$	0.308	0.321
$x = 0.06$	0.331	0.338
$x = 0.08$	0.341	0.343
$x = 0.10$	0.315	0.318

4. Conclusions

Novel Dy^{3+}-doped $GdPO_4$ white light phosphors with monoclinic system were successfully synthesized by hydrothermal method at 240 °C. The strong absorption at around 147 nm in excitation spectrum energy can easily be transferred to the energy levels of Dy^{3+} ion from the host absorption. The f–d transition of Dy^{3+} ion was observed to be located at 182 nm which consisted with the calculated value using Dorenbos' expression. Two strong emission bands locating at 572 nm and 478 nm under 147 nm excitation were observed, which results in that the chromaticity coordinates of $Gd_{1-x}PO_4 : xDy^{3+}$ phosphors are located in the white-light region. Additionally, this white light phosphors are activated by a single Dy^{3+} ion and with a lower preparation temperature, which tend to decrease the consumption of RE resource and energy. Therefore, the luminescence of $Gd_{1-x}PO_4 : xDy^{3+}$ under VUV excitation was effective, and it is promising to be applied to mercury-free lamp.

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