Novel Dy^{3+}-doped $Gd(PO_3)_3$ white-light phosphors under VUV excitation for Hg-free lamps application*

Zhang Li(张 锂)[a] and Han Guo-Cai (韩国才)[b]†

[a] Department of Basic Course, Lanzhou Institute of Technology, Lanzhou 730050, China
[b] Department of Material Engineering, Lanzhou Institute of Technology, Lanzhou 730050, China

(Received 26 April 2012; revised manuscript received 7 July 2012)

Novel Dy^{3+}-doped $Gd(PO_3)_3$ white light phosphors each with an orthorhombic system are successfully synthesized by solid-state reaction. The luminescence properties of white-light $Gd_{1-x}(PO_3)_3$:xDy^{3+} ($0 < x \leq 0.25$) under vacuum ultraviolet (VUV) excitation are investigated. 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, the white light phosphor is activated by a single Dy^{3+} ion. Therefore, the luminescence of $Gd_{1-x}(PO_3)_3$:xDy ($0 < x \leq 0.25$) under VUV excitation is effective, and it has the promise of being applied to mercury-free lamps.

Keywords: vacuum ultraviolet, white light, phosphors

PACS: 78.55.–m, 78.66.–w **DOI:** 10.1088/1674-1056/22/2/027803

1. Introduction

Recently, luminescence materials doped with Dy^{3+} have drawn much attention for their white emissions.[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 the other 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+}-active luminescence material. Therefore Dy^{3+}-activated phosphors are promising white light phosphors and can be used in mercury-free lamps. For a mercury-free lamp, the excitation energy is mainly composed of VUV radiation, but most of the VUV energy is absorbed by the host crystal. If the energy can be transferred from the host to the rare earth ions, the rare earth ions can emit visible light. So the host absorption efficiency and the energy transfer efficiency play a very important part in applying VUV-excited phosphors to the mercury-free lamp.

Rare-earth-ion-doped phosphate-based phosphors have been used in various fields, such as plasma display panels (PDP), mercury-free lamps, and visible lasers.[1–5] It can be concluded that orthophosphates are promising host materials for their applications in the VUV region.[6,7]

$Ln(PO_3)_3$ (Ln = La to Gd) complex polyphosphates and $Ln(PO_3)_3$ with large rare-earth ions (La to Gd) each crystallize into an orthorhombic crystal structure.[8] We have investigated the luminescence properties of La $(PO_3)_3$:Tb under 172-nm excitation and found that the $(PO_3)_3^{3-}$ groups can efficiently absorb the excited energy around 174 nm.[9] The optimum emission intensity of the VUV excitation spectrum of $La_{0.55}(PO_3)^{3-}$:$Tb^{3+}_{0.45}$ indicates that the absorptions of the $(PO_3)_3^{3-}$ group are located at about 163 nm and 174 nm and the absorption bands of the $(PO_3)_3^{3-}$ group at 174 nm. These results imply that the $(PO_3)_3^{3-}$ group can efficiently absorb the excited energy around 172 nm and transfer the energy to Tb^{3+}. Thus we confirm that orthorhombic $(PO_3)_3^{3-}$ is a promising host under VUV excitation, too.

In this work, we synthesize Dy^{3+}-doped $Gd(PO_3)_3$ phosphors by the solid-state reaction. Meanwhile, photoluminescence properties of Dy^{3+}-doped $Gd(PO_3)_3$ phosphor in the VUV region are also investigated.

2. Experimental procedure

Preparation of $Gd_{1-x}(PO_3)_3$:xDy^{3+} ($0 < x \leq 0.25$) by solid-state reaction is as follows. First, the purity of $(NH_4)_2HPO_4$ is AR, and the purities of Gd_2O_3 and Dy_2O_3 are both better than 99.99%. The value of doping content x of Dy_2O_3 ranges from 0.05% to 0.25%. Appropriately high-purity $(NH_4)_2HPO_4$, Gd_2O_3, and Dy_2O_3 were thoroughly mixed and ground together; a 5% excess of the $(NH_4)_2HPO_4$ was used to compensate for the evaporation of the $(NH_4)_2HPO_4$ at high temperature in solid-state reactions. The mixture was heated at 400 °C for 1 h and the mixture was heated again at 700 °C for 1 h, reground and reheated at the temperature of 1150 °C for 4 h.

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

*Project supported by the National Natural Science Foundation for Young Scientists of China (Grant No. 502041032).
†Corresponding author. E-mail: hgclzu@163.com
© 2013 Chinese Physical Society and IOP Publishing Ltd

The excitation and emission spectra were measured using an Edinburgh Instruments FLS920T. The scan speed was 30 nm/m in steps 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 X-ray diffraction pattern of the typical sample $Gd_{1-x}(PO_3)_3{:}xDy^{3+}$ $(0 < x \leq 0.25)$ is shown in Fig. 1. All diffraction peaks can be well matched with those of standard card JCPDS 52-1761. It indicates the samples are single phase.

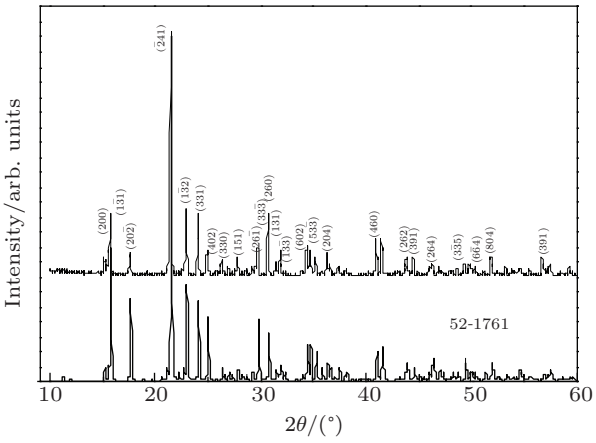


Fig. 1. The X-ray powder diffraction patterns of $Gd_{0.90}(PO_3)_3{:}0.10Dy^{3+}$.

Figure 2 shows emission spectra of $Gd_{1-x}(PO_3)_3{:}xDy^{3+}$ $(0 < x \leq 0.25)$ under 147-nm excitation. From Fig. 2, the peaks at 406 nm, 462 nm, 482 nm, 578 nm, and 660 nm can be attributed to transitions $^4F_{7/2}$–$^6H_{15/2}$, $^4F_{7/2}$–$^6H_{13/2}$, $^4F_{9/2}$–$^6H_{15/2}$, $^4F_{9/2}$–$^6H_{13/2}$, and $^4F_{9/2}$–$^6H_{11/2}$ of Dy^{3+}, respectively. These attributions are similar to those of the other systems in Refs. [10] and [11]. Transition $^4F_{9/2}$–$^6H_{15/2}$ is mainly allowed in magnitude and hardly varies with the environment, while transition $^4F_{9/2}$–$^6H_{13/2}$ (yellow) belongs to hypersensitive transition and is strongly influenced by outside surroundings.[12–14] Their relative intensity depends strongly on the local symmetry of Dy^{3+}, and a lower symmetry local site will result in a higher ratio of yellow to blue as shown in Ref. [15]. From our result, the ratio of yellow to blue is larger than 1, indicating that the site Dy^{3+} is located with lower symmetry. In the samples, it is obvious that the intensities of the peaks at 482 nm and 578 nm are gradually enhanced with the increase of x and become dominant when $x = 0.10$, then decrease when $x > 0.10$. Therefore, by adjusting the yellow-to-blue intensity ratio (Y/B) value, the chromaticity coordinates in the white light zone of $Gd_{1-x}(PO_3)_3{:}xDy^{3+}$ $(0 < x \leq 0.25)$ phosphors can be obtained.

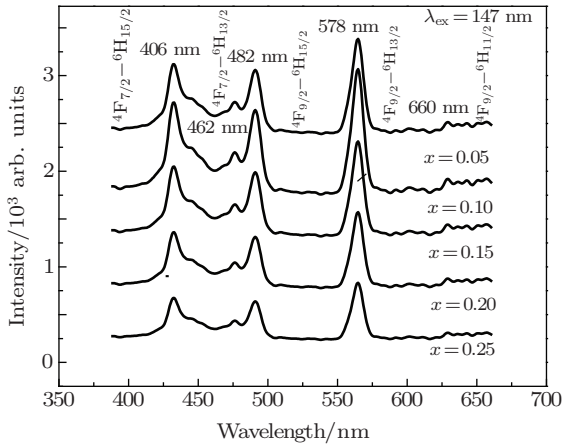


Fig. 2. Emission spectra of $Gd_{1-x}(PO_3)_3{:}xDy^{3+}$ $(0 < x \leq 0.25)$.

Figure 3 shows the variation of luminescence intensity of the main emission peak at 578 nm with the increase of doping concentration x of $Gd_{1-x}(PO_3)_3{:}xDy^{3+}$ $(0 < x \leq 0.25)$. From Fig. 3, it is clear that the luminescence intensity of $Gd_{1-x}(PO_3)_3{:}xDy^{3+}$ $(0 < x \leq 0.25)$ increases with the increase of x and when $x = 0.10$, the luminescence intensity is strongest.

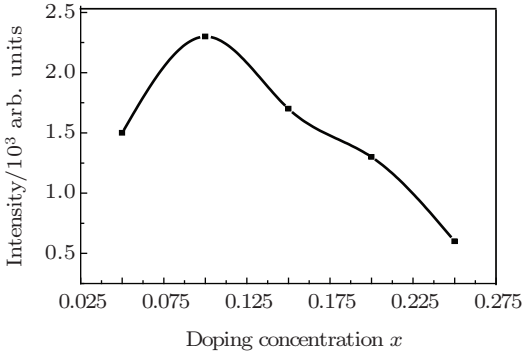


Fig. 3. Variation of luminescence intensity of the main emission peak at 578 nm with doping amount x.

Figure 4 shows the excitation spectrum of $Gd_{0.9}(PO_3)_3{:}0.10Dy^{3+}$ monitored at 578 nm. In the excitation spectrum, the broad band ranging from 125 nm to 165 nm can be attributed to the host absorption of polyphosphate, and there have been similar observations in other systems in Refs. [8], [9], [16], and [17]. The band at around 179 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 Dorenbos's expression[18,19]

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

where $E(\mathrm{Ln}, A)$ is the f–d energy difference in units of cm^{-1} of lanthanide ion Ln^{3+} doped in compound A with the so-called crystal field depression $D(A)$; 49340 cm^{-1} is the energy of the first f–d transition of Ce^{3+} as a free (gaseous) ion; $\Delta E^{\mathrm{Ln,Ce}}$

is defined as the difference between the f–d energy of Ln^{3+} and that of the first electric dipole allowed transition in Ce^{3+}. In Ref. [19] , $D(A)$ is 16007 cm^{-1} ($Gd(PO_3)_3$), and $\Delta E^{Ln,Ce}$ is (25100±610) cm^{-1}. Therefore, by Eq. (1), we can calculate the f–d transition position of Dy^{3+} in the system to be (171±2) nm, which is close to that shown in Fig. 4.[20,21]

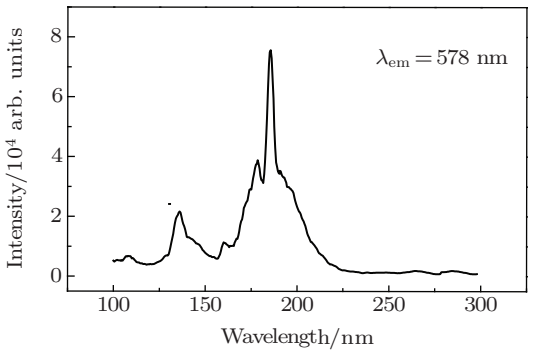


Fig. 4. Excitation spectrum of $Gd_{1-x}(PO_3)_3{:}xDy^{3+}$ ($x = 0.10$).

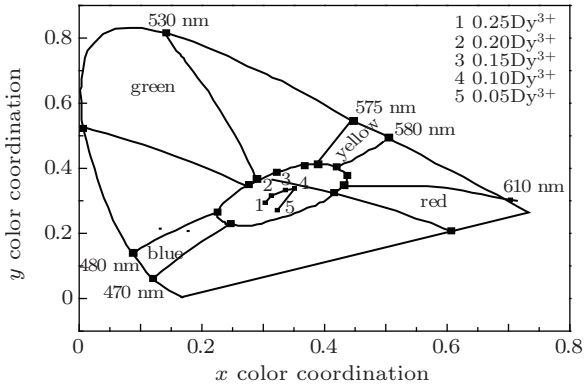


Fig. 5. Chromaticity coordinates (x, y) of $Gd_{1-x}(PO_3)_3{:}xDy^{3+}$ ($0 < x \leq 0.25$) under 147-nm excitation in the CIE 1931 chromaticity diagram.

Table 1. Chromaticity coordinates of $Gd_{1-x}(PO_3)_3{:}xDy^{3+}$ ($0 < x \leq 0.25$).

The amount of doping x	The chromaticity coordinate x	The chromaticity coordinate y
$x = 0.25$	0.298	0.299
$x = 0.20$	0.308	0.321
$x = 0.15$	0.329	0.338
$x = 0.10$	0.339	0.348
$x = 0.05$	0.300	0.288

Figure 5 shows the chromaticity coordinate (x, y) of $Gd_{1-x}(PO_3)_3{:}xDy^{3+}$ ($0 < x \leq 0.25$) excited under 147 nm in the CIE 1931 chromaticity diagram. It is obvious that the chromaticity coordinates of $Gd_{1-x}(PO_3)_3{:}xDy^{3+}$ ($0 < x \leq 0.25$) gradually moves to the warm white side and approaches the yellow region with the decrease of x; when $x > 0.10$, it moves to the cold white side toward the contrary direction which can arise from the ratio between the luminescence intensity of the peak located at 482 nm and that at 578 nm. Detailed chromaticity coordinates are shown in Table 1, which are located in the white light region.

4. Conclusions

Novel Dy^{3+}-doped $Gd(PO_3)_3$ white light phosphors each with an orthorhombic system are successfully synthesized by solid-state reaction. The strong absorption at around 147 nm in excitation spectrum energy can easily be transferred to the energy levels of the Dy^{3+} ion from the host absorption. The f–d transition of the Dy^{3+} ion is observed at 179 nm which is consistent with the calculated value using Dorenbos's expression. Two strong emission bands located, respectively, at 482 nm and 578 nm under 147-nm excitation are observed, which results in the chromaticity coordinates of $Gd_{1-x}(PO_3)_3{:}xDy^{3+}$ ($0 < x \leq 0.25$) phosphors being located in the white-light region. Additionally, this white light phosphor is activated by a single Dy^{3+} ion and with solid-state reaction. Therefore, the luminescences of $Gd_{1-x}(PO_3)_3{:}xDy^{3+}$ ($0 < x \leq 0.25$) under VUV excitation are effective, and have the promise of being applied to mercury-free lamps.

Acknowledgment

The computer resources were provided by the Department of Basic Course, Lanzhou Institute of Technology, Lanzhou 730050, China.

References

[1] Chen X B, Zhang G Y, Chen J K, Wang H, Liu Y B, Shang M R and Li J W 1993 *Acta Phys. Sin.* (Overseas Edition, i.e. *Chin. Phys.*) **2** 695
[2] Liang X L, Zhu C F, Yang Y X, Yuan S L and Chen G R 2008 *J. Lumin.* **128** 1162
[3] Zhang J C and Wang Y H 2008 *Chin. Phys. Lett.* **25** 1453
[4] Su X Q and Yan B 2005 *Mater. Chem. Phys.* **93** 552
[5] Wang Y H, Wu C F and Wei J 2007 *J. Lumin.* **126** 503
[6] Li Y and Hong G 2005 *J. Lumin.* **26** 587
[7] Jstel T, Krupa J C and Wiechert D U 2001 *J. Lumin.* **93** 179
[8] Wang D, Wang Y H and Wang L L 2007 *J. Electrochem. Soc.* **154** J32
[9] Wang Y H and Wang D 2007 *J. Solid-State Chem.* **180** 3450
[10] Li Y C, Chang Y H, Lin Y F, Chang Y S and Lin Y J 2007 *J. Alloys Compd.* **439** 367
[11] Bao A, Yang H, Tao C Y, Zhang Y and Han L L 2006 *J. Lumin.* **128** 60
[12] Chen L M, Liu G C, Liu Y N and Huang K L 2008 *J. Materials Processing Technology* **198** 129
[13] Yh M, Lin J, Fu J, Wang S, Zhang H J and Han Y C 1994 *J. Alloys Compd.* 210 159
[14] Jun L and Qiang S 2002 *Chem. Mater.* **14** 2224
[15] Mini K K, Anoop G and Jayaraj M K 2007 *J. Electrochem. Soc.* **154** J310
[16] Wu C F, Wang Y and Wang D 2008 *Electrochem. Solid-State Lett.* **11** J9
[17] Dorenbos P 2000 *J. Lumin.* **91** 91
[18] Yang H C, Li C Y, He H, Tao Y, Xu J H and Su Q 2006 *J. Lumin.* **118** 61
[19] Su Q, Liang H B, Li C Y, He H, Lu Y H, Li J and Tao Y 2007 *J. Lumin.* **122–123** 927
[20] He H, Liang H B, Wang S B, Su Q, Tao Y, Ju X and Hou X Y 2002 *Nuclear Technig.* **25** 783
[21] Zhang J P, Liang H B, Han B, Tian Z F and Su Q 2008 *Opt. Express* **16** 750