

Research Article

The High-Temperature Synthesis of the Nanoscaled White-Light Phosphors Applied in the White-Light LEDs

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The white-light phosphors consisting of Dy^{3+} doped YPO_4 and Dy^{3+} doped $YP_{1-x}V_xO_4$ were prepared by the chemical coprecipitation method. After the $1200^\circ C$ thermal treatment in the air atmosphere, the white-light phosphors with particle sizes around 90 nm can be obtained. In order to reduce the average particle size of phosphors, the alkaline washing method was applied to the original synthesis process, which reduces the particle sizes to 65 nm. From the PLE spectra, four absorption peaks locating at 325, 352, 366, and 390 nm can be observed in the YPO_4 -based phosphors. These peaks appear due to the following electron transitions: ${}^6H_{15/2} \rightarrow {}^4K_{15/2}$, ${}^6H_{15/2} \rightarrow {}^4M_{15/2}+{}^6P_{7/2}$, ${}^6H_{15/2} \rightarrow {}^4I_{11/2}$, and ${}^6H_{15/2} \rightarrow {}^4M_{19/2}$. Besides, the emission peaks of wavelengths 484 nm and 576 nm can be observed in the PL spectra. In order to obtain the white-light phosphors, the vanadium ions were applied to substitute the phosphorus ions to compose the $YP_{1-x}V_xO_4$ phosphors. From the PL spectra, the strongest PL intensity can be obtained with 30% vanadium ions. As the concentration of vanadium ions increases to 40%, the phosphors with the CIE coordinates locating at the white-light area can be obtained.

1. Introduction

Due to the excellent luminescent properties and chemical stabilities, the phosphors using yttrium vanadate (YVO_4) and yttrium phosphate (YPO_4) as the host materials have been used in a broad range of daily life, such as the cathode ray tubes, electroluminescence devices, field emission displays, plasma display panels, projection displays, and ultraviolet light-emitting diodes (UV-LEDs) [1–4]. The europium (Eu^{3+}) doped YVO_4 phosphor especially is one of the excellent commercial red-light phosphors, which has been studied for many years [5–9]. In addition to the Eu^{3+} ions, the phosphor doped with dysprosium (Dy^{3+}) ions is also a potential luminescent material. The active center Dy^{3+} can yield two emission bands: the yellow-light band and the blue-light band, and these two emission bands originate from the transition ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ and the transition ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$, respectively.

Through adjusting the relative intensities of yellow-light band and blue-light band, it is possible to obtain

the white-light phosphors [8, 10–12]. Owing to the same crystal structure, similar lattice constants, and similar physical and chemical properties between YPO_4 and YVO_4 phosphors, the material $Y(P,V)O_4$ has been paid much attention to in recent decades [13–15].

In accordance with the above advantages, different synthesis methods were applied to produce the $Y(P,V)O_4$ phosphors in recent years. Bao et al. synthesized the phosphors via the sol-gel method in 2008; the average particle size is around 80 nm with the $1000^\circ C$ thermal treatment [16]. In 2009, Nguyen et al. applied the hydrothermal method to produce the $Y(P,V)O_4$ phosphors, under the $1000^\circ C$ synthesis temperature; the particle sizes are around 70 to 90 nm [17]. Additionally, the solid-state method is also a common method to synthesize the phosphors. Under the $1200^\circ C$ thermal treatment for 6 hours, the phosphors with particle sizes around 2 to $4\ \mu m$ can be obtained [18]. The methods above are either complicated or larger particle sizes. In this research, the chemical coprecipitation method with thermal treatments is adopted to synthesize the phosphors. In 2005, Su and Yanever used the similar processes to synthesize

the Y(P,V)O₄ phosphors at 1100°C, but the average particle sizes are around 0.5 to 2 μm [19]. In order to reduce the particle sizes, the alkaline-washing method was applied to the chemical coprecipitation method in this research and it can reduce the average particle size to 65 nm effectively.

2. Materials and Methods

In this study, yttrium nitrate hexahydrate Y(NO₃)₃·6H₂O (99.9%, Alfa Aesar), dysprosium nitrate pentahydrate Dy(NO₃)₃·5H₂O (99.9%, Alfa Aesar), phosphoric acid H₃PO₄ (85%, Panreac), and ammonium vanadate NH₄VO₃ (99.5%, Acros Organics) were used as the starting materials. At first, Y(NO₃)₃·6H₂O, Dy(NO₃)₃·5H₂O and H₃PO₄ were dissolved into distilled water by the stoichiometric ratio and the mixed solution was stirred for an hour at room temperature. Secondly, ammonia was used as the precipitant and added into the above solution. With the addition of ammonia, the pH value of mixed solution was adjusted to 8.0, and this solution was placed for 12 hours. After 12 hours, the white precipitation could be observed and separated directly by a centrifuge. Thirdly, the precipitation was washed by distilled water and ethanol for several times. Finally, the dried precipitation was used as the precursor to synthesize the YPO₄:Dy³⁺ and YP_{1-x}V_xO₄:Dy³⁺ phosphors by the suitable thermal treatment in the air atmosphere for 1 hour.

Alkaline washing process: the precipitation was washed with ammonia and dried directly. Then, the dried powders can be used as the precursor.

The X-ray diffraction patterns of phosphors were collected by Rigaku Miniflex II desktop X-ray diffractometer with Cu-Kα radiation. The particle morphology was studied by a field emission scanning electron microscope (FESEM, JEOL JSM-6500F). And the optical properties were studied with a fluorescence spectrophotometer (Hitachi F-2700PL).

3. Results and Discussion

Figure 1 shows the XRD patterns of YPO₄ phosphors with different thermal treatments. It can be seen from this figure that the three predominant peaks locating at 2θ = 25.9°, 35.0°, and 51.8° appear due to the following diffraction planes: (200), (112), and (312) of YPO₄. Comparing with the JCPDS standard card (number 11-0254), the crystalline structures of all YPO₄ phosphors prepared through the chemical coprecipitation method are confirmed as the tetragonal structures. No impurity phases resulting from the starting materials can be observed. As the thermal treatment temperature increases, the better crystallinity can be obtained.

The scanning electron microscope (SEM) images are shown in Figure 2. The irregular shape and agglomeration phenomenon of nanoparticles can be observed. The average particle size of phosphors is about 90 nm with the 1200°C thermal treatment and the agglomeration of phosphors is serious. From Figure 2(b), the particle size of phosphors reduces to 65 nm with the alkaline washing process and this process can also improve the agglomeration of phosphors.

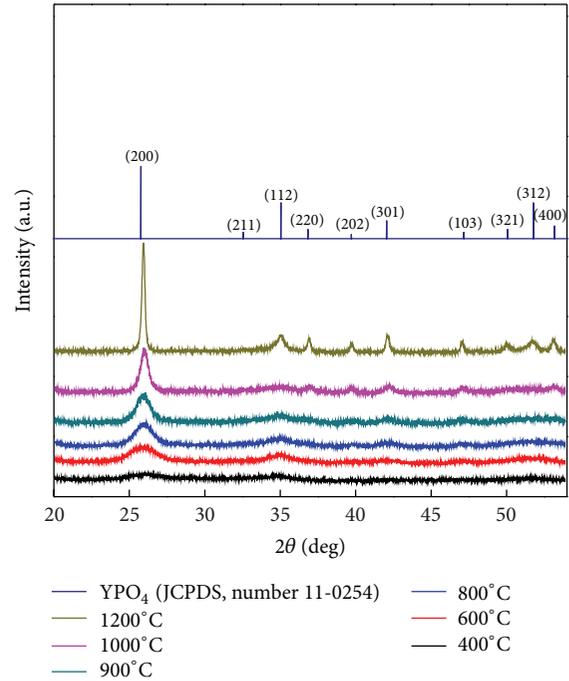
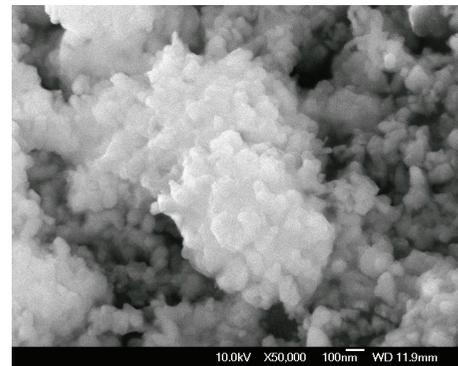
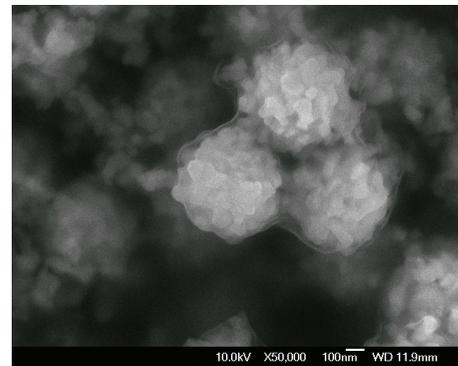


FIGURE 1: The XRD patterns of YPO₄ phosphors with different thermal treatments.



(a)



(b)

FIGURE 2: The SEM images of YPO₄ phosphors with the 1200°C thermal treatment. (a) 1200°C. (b) 1200°C with the alkaline-washing process.

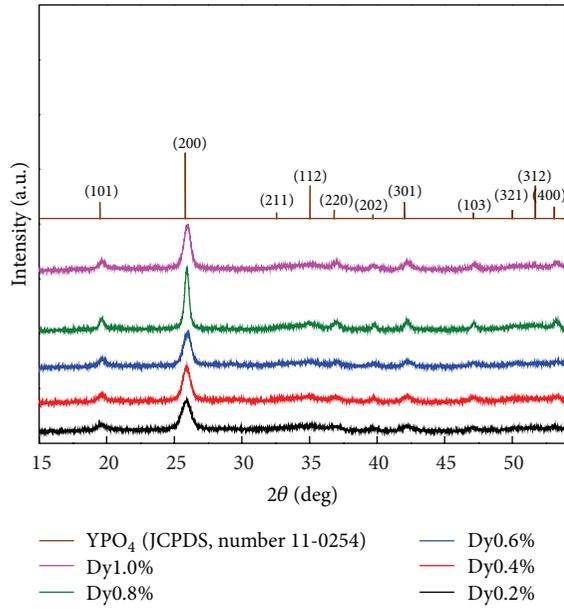


FIGURE 3: The XRD patterns of YPO_4 phosphors with different dopant concentrations.

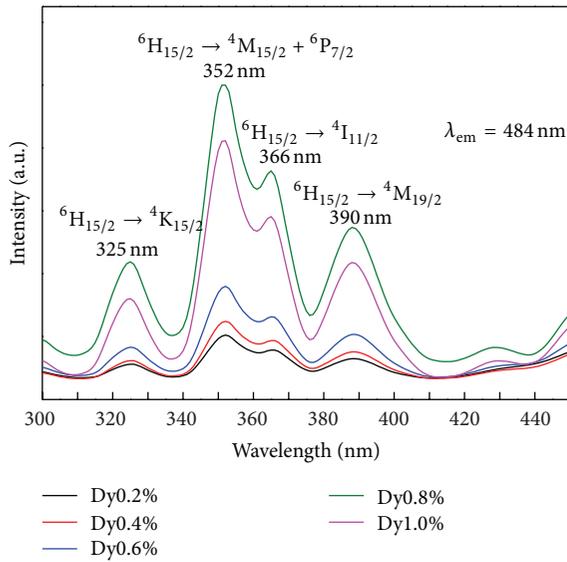


FIGURE 4: The PLE spectra of $\text{YPO}_4:\text{Dy}^{3+}$ phosphors with different dopant concentrations, $\lambda_{\text{em}} = 484 \text{ nm}$.

Figure 3 shows the XRD patterns of YPO_4 phosphors with different dopant concentrations. In this figure, the lattice constants of phosphors change with the dopant concentrations, but all XRD patterns still exhibit the tetragonal structure. Small enlargement in the lattice constants of the $\text{YPO}_4:\text{Dy}^{3+}$ from YPO_4 occurs due to the presence of Dy^{3+} (ionic radii of Dy^{3+} and Y^{3+} are 0.912 Å and 0.900 Å, resp.). The PLE spectra of $\text{YPO}_4:\text{Dy}^{3+}$ phosphors are revealed in Figure 4 with the emission wavelength (λ_{em}) 484 nm. Four absorption peaks can be observed from the PLE spectra. The 325 nm absorption peak originates from the f-f transition ${}^6\text{H}_{15/2} \rightarrow {}^4\text{K}_{15/2}$

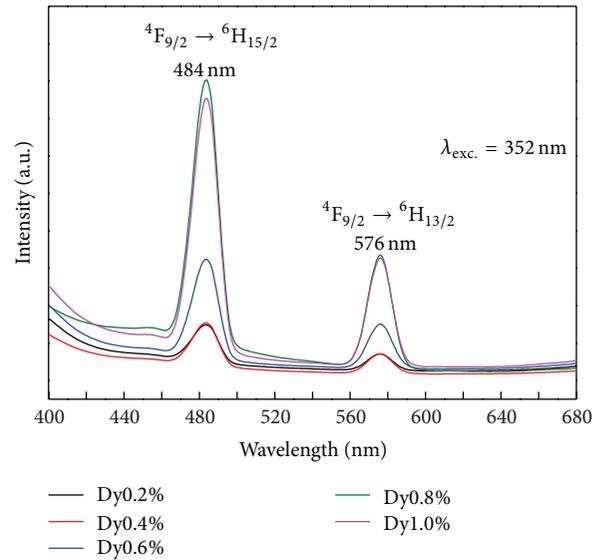


FIGURE 5: The PL spectra of $\text{YPO}_4:\text{Dy}^{3+}$ phosphors with different dopant concentrations, $\lambda_{\text{exc}} = 352 \text{ nm}$.

within Dy^{3+} . And the 352 nm, 366 nm, and 390 nm absorption peaks appear because of the following transitions: ${}^6\text{H}_{15/2} \rightarrow {}^4\text{M}_{15/2} + {}^4\text{P}_{7/2}$, ${}^6\text{H}_{15/2} \rightarrow {}^4\text{I}_{11/2}$, and ${}^6\text{H}_{15/2} \rightarrow {}^4\text{M}_{19/2}$, respectively. Herein, the 352 nm peak is the strongest absorption peak of all peaks and is chosen as the excitation wavelength in the following PL measurements.

Figure 5 demonstrates the PL spectra of $\text{YPO}_4:\text{Dy}^{3+}$ phosphors. Two emission peaks can be observed from the PL spectra. The 484 nm peak is the result from the transition ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ and the 576 nm peak occurs as the result of the transition ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$. The PL intensity increases with the Dy^{3+} ion concentration. As the Dy^{3+} ion concentration increases to 0.8%, the phosphor can possess the strongest luminescent property. When the dopant concentration is above 0.8%, the concentration quench effect can be observed obviously.

Figure 6 shows the XRD patterns of $\text{Y}_{0.992}\text{P}_{1-x}\text{V}_x\text{O}_4:0.008\text{Dy}^{3+}$ phosphors. The x means vanadium ion concentration and it starts from 0.1 to 0.5. As mentioned in [18], the cell parameters of YPO_4 are $a = b = 6.8817 \text{ Å}$; $c = 6.0177 \text{ Å}$ and those of YVO_4 are $a = b = 7.1183 \text{ Å}$; $c = 6.2893 \text{ Å}$. When the concentration of vanadium ions increases, the angles of all diffraction peaks tend to be smaller (ionic radii of P^{5+} and V^{5+} are 0.34 Å and 0.59 Å, resp.). The lattice constant of $\text{Y}_{0.992}\text{P}_{1-x}\text{V}_x\text{O}_4:0.008\text{Dy}^{3+}$ phosphor increases close to the lattice constant of YVO_4 with vanadium quantity. Three predominant peaks locating at 25.4°, 34.2°, and 50.6° result from the diffraction planes (200), (112), and (312). The almost similar XRD patterns indicate that the presence of V^{5+} does not affect the crystal structure of the $\text{Y(P,V)}\text{O}_4$ phosphors.

The PLE spectra of $\text{Y}_{0.992}\text{P}_{1-x}\text{V}_x\text{O}_4:0.008\text{Dy}^{3+}$ phosphors are shown in Figure 7. With the emission wavelength 484 nm, 3 absorption peaks locating at 352, 366, and 390 nm

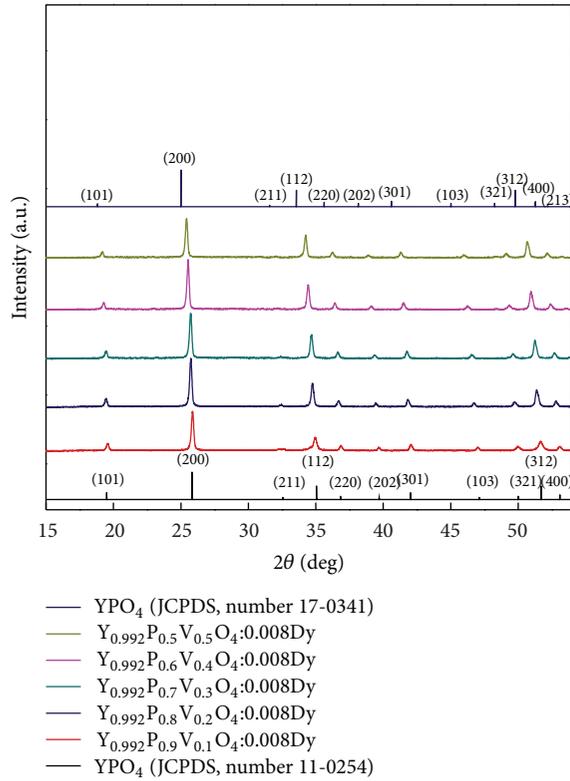


FIGURE 6: The XRD patterns of $Y_{0.992}P_{1-X}V_XO_4:0.008Dy^{3+}$ phosphors ($X = 1$ to 0.5).

can be observed. These peaks are the results of the following electron transitions: ${}^6H_{15/2} \rightarrow {}^4M_{15/2} + {}^6P_{7/2}$, ${}^6H_{15/2} \rightarrow {}^4I_{11/2}$ and ${}^6H_{15/2} \rightarrow {}^4M_{19/2}$, respectively. The 352 nm absorption peak is still the strongest absorption peak of all and is chosen as the excitation wavelength for the PL measurements. Figure 8 shows the PL spectra of $Y_{0.992}P_{1-X}V_XO_4:0.008Dy^{3+}$ phosphors. These two emission peaks locating at 484 nm and 576 nm can be observed in the PL spectra. These two peaks originate from the electron transitions ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ and ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$, respectively. As the concentration of vanadium ions increases, the PL intensity increases. When the vanadium concentration reaches 30%, the phosphor can possess the best emission property. According to the CIE coordinates in Figure 9, the phosphor $Y_{0.992}PO_4:0.008Dy^{3+}$ can be used as a blue-white phosphor. With the addition of vanadium ions, the CIE coordinates can be adjusted to the white-light area. From Figure 9(b), the coordinates of phosphors with 40% and 50% vanadium concentration locate at (0.269, 0.317) and (0.279, 0.327).

4. Conclusion

The white-light phosphors with average particle size 90 nm can be obtained through the chemical coprecipitation method with suitable thermal treatments in this study. The alkaline-washing process was applied to the original synthesis

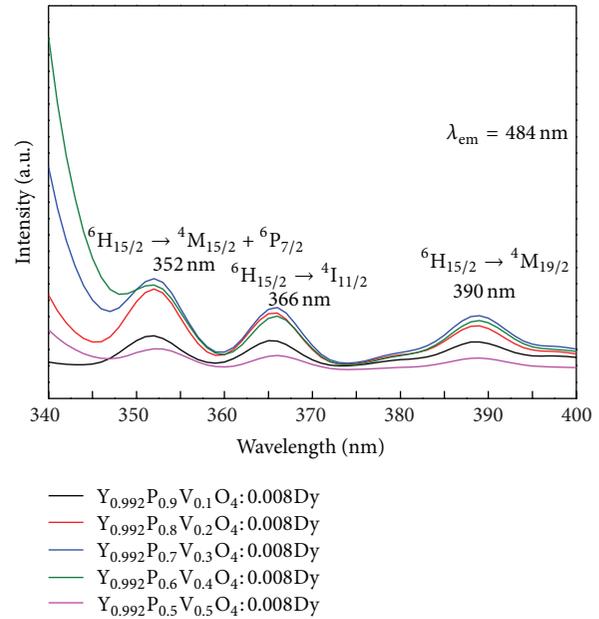


FIGURE 7: The PLE spectra of $Y_{0.992}P_{1-X}V_XO_4:0.008Dy^{3+}$ phosphors ($X = 1$ to 0.5), $\lambda_{em} = 484$ nm.

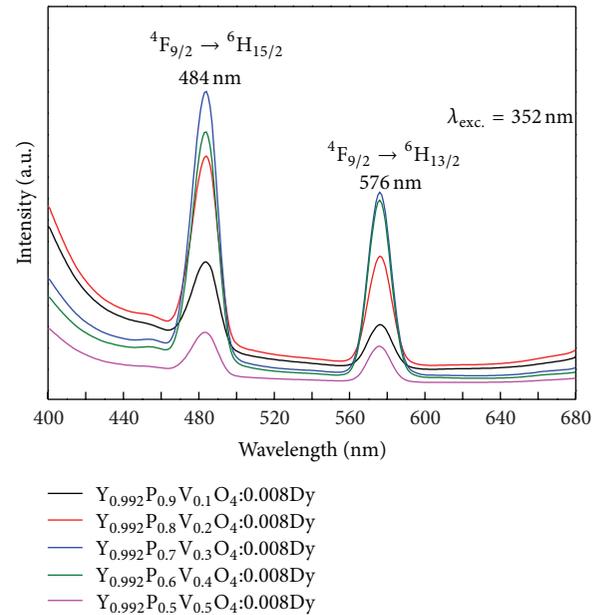


FIGURE 8: The PL spectra of $Y_{0.992}P_{1-X}V_XO_4:0.008Dy^{3+}$ phosphors ($X = 1$ to 0.5), $\lambda_{exc} = 352$ nm.

to reduce the average particle size. In this research, the particle size of phosphors can be reduced to 65 nm through the alkaline washing process and this process can also improve the agglomeration phenomenon. From the XRD patterns, the YPO_4 phosphors with different thermal treatments all crystallize into the tetragonal structure. The lattice constant increases with the concentration of vanadium ions and tends to the lattice constant of YVO_4 . There are four absorption peaks observed in the PLE spectra, which are the results

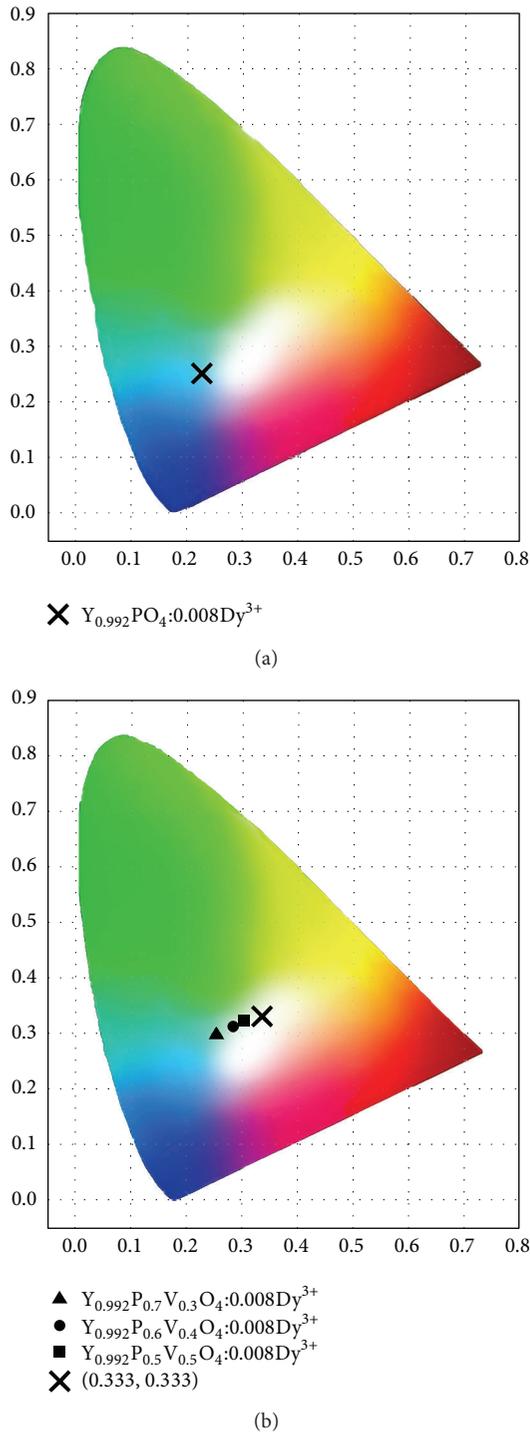


FIGURE 9: The CIE coordinates of (a) $YPO_4:Dy^{3+}$ phosphor and (b) $Y(P,V)O_4:Dy^{3+}$ phosphors.

of the transitions ${}^6H_{15/2} \rightarrow {}^4K_{15/2}$, ${}^6H_{15/2} \rightarrow {}^4M_{15/2} + {}^4P_{7/2}$, ${}^6H_{15/2} \rightarrow {}^4I_{11/2}$, and ${}^6H_{15/2} \rightarrow {}^4M_{19/2}$. Additionally, two emission peaks locating at 484 nm and 576 nm can be observed in the PL spectra and they originate from the electron transitions, ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ and ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$, respectively. By substituting the vanadium ions for the

phosphorus ions in YPO_4 phosphors, the relative intensities of these two emission peaks can be tuned to produce the white-light phosphor. The 40% vanadium concentration is the optimal condition to obtain the white-light phosphor $Y_{0.992}P_{0.6}V_{0.4}O_4:0.008Dy^{3+}$ in our work. It is believed that the chemical coprecipitation method with thermal treatments is an effective way to obtain the white-light phosphors.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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