

Photoluminescence characteristics of $(\text{Y,Gd})\text{P}_{0.5}\text{V}_{0.5}\text{O}_4:\text{Tm}^{3+}$ phosphor particles prepared by coprecipitation reaction

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Abstract

A novel blue-emitting material, fine-particle phosphor $(\text{Y,Gd})\text{P}_{0.5}\text{V}_{0.5}\text{O}_4:\text{Tm}^{3+}$, has been prepared via co-precipitation reaction. The phosphor particles were characterized by XRD, SEM, and photoluminescence under vacuum ultraviolet (VUV, 147 nm) or ultraviolet (UV, 254 nm) excitation. The XRD patterns disclosed that $(\text{Y,Gd})\text{P}_{0.5}\text{V}_{0.5}\text{O}_4:\text{Tm}^{3+}$ particles calcined at 1200 °C have the highest intensity. The SEM image showed that the size of the phosphor particles is uniform and submicron, and their morphology is regular and no agglomeration found. The fine particles blue-emitting material exhibits a narrow emission peak at 475 nm and a weak broad-band around 430 nm, whose intensity is dependent on the contents of Tm^{3+} and VO_4^{3-} .

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1. Introduction

The plasma display panel (PDP) has been edged competitively in the market of large flat panel display, yet much improvement concerning the luminescent efficiency, lifetime, and color purity of the phosphors is still in need. Particularly, superior display performance of the PDP device requires further improvement in morphology, particle size, particle size distribution, luminescent efficiency, and luminescent lifetime, and stability of phosphors. Usually, the commercial PDP phosphors are produced by using the solid-state reactions at high temperature, however, it is difficult to control over the particle size and morphology, uniform dopant concentration. Compared to the conventional solid-state reaction process, some aerosol synthesis techniques such as spray py-

rolysis and coprecipitation reaction have been suggested the better ways to obtain PDP phosphors provided with improved morphology and particle size. In recent years much work reported that phosphor particles with good morphology have been synthesized successfully using these aerosol synthesis techniques [1–4].

The commercial PDP blue-emitting phosphor $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ represented good enough spectral properties but its easy-aging has been puzzling researchers in practical application. In order to recognize the aging mechanism of the blue emitting phosphor $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$, extended investigations have been completed. Nowadays it is very clear that lattice deformation of the host and oxidation of the divalent europium ions are the main reason causing the phosphor aging [5–7]. Facing these aging mechanism of the blue emitting phosphor, we could propose an approach to improve phosphor performance that selecting a novel stable host, in which Eu^{2+} can be stably existent and have excellent spectral

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properties for the PDP application. Otherwise, it is also a good idea that looking for a new luminescent center with unvaried valence to substitute for Eu^{2+} . In the lanthanide series, Tm^{3+} may be a feasible candidate for the blue emissions originating from $^1\text{D}_2 \rightarrow ^3\text{H}_4$ (around 450 nm), $^1\text{G}_4 \rightarrow ^3\text{H}_6$ (around 480 nm) transitions. The present work is a primary try for finding a novel candidate of blue emitting PDP phosphor.

As for their high-energy optical absorption in VUV, yttrium orthovanadate (YVO_4) and yttrium orthophosphate (YPO_4) were selected usually as host materials [8–11]. Tm^{3+} ion is selected as a blue-emitting activator according to its energy level and stability under the operating condition in PDP devices. The phosphor $(\text{Y,Gd})\text{P}_{0.5}\text{V}_{0.5}\text{O}_4:\text{Tm}^{3+}$ particles were prepared via coprecipitation reaction. The dependence of XRD patterns on the post treatment temperature was observed. TEM photo was taken for the sample after post treatment. The emission spectra were measured under VUV excitation for the samples with different Tm^{3+} concentration. The dependence of emission spectra on the post treatment temperature was observed.

2. Experimental

According to a certain stoichiometric ratio, yttrium oxide (Y_2O_3 99.99%, AR), Gadolinium oxide (Gd_2O_3 99.99%, AR), Thulium oxide (Tm_2O_3 99.99%, AR) and vanadium pentoxide (V_2O_5 99%, AR) were weighed and dissolved in hydrochloric acid. The mixture was heated and stirred in a hot beaker at 70–80 °C, then added another mixture of hydrogen peroxide solution (H_2O_2 , AR), ammonia spirit (NH_4OH , AR), diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$, AR) solution. The precipitate was washed by de-ionized water and filtrated. Finally, the white phosphor $(\text{Y,Gd})\text{P}_{0.5}\text{V}_{0.5}\text{O}_4:\text{Tm}^{3+}$ was obtained when the precipitate was dried at 120 °C for 12 h and calcined at a appropriate temperature for 2 h.

The samples were characterized with X-ray diffraction (XRD, RIGAKU, D/MAX-II B) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178$), scanning electron microscope (SEM, AMARY, KYKY-1000B), ultraviolet (UV, HITACH, F4500) and vacuum ultraviolet (VUV, FEXEM-SKLAO100 with VM502 monochromator and 30 W deuterium discharge lamp) spectra.

3. Results and discussion

YVO_4 and YPO_4 have the similar structure of ZrSiO_4 with slight difference in lattice parameters [12]. YVO_4 and YPO_4 can form the same solid solution [13] that can be used as luminescence host doped with Eu^{3+} , Dy^{3+} , etc. [9,14]. Furthermore, the structure of YVO_4 crystal has no changes when V^{5+} is substituted for P^{5+} partly [15]. Fig. 1 shows the XRD patterns of $(\text{Y,Gd})\text{P}_{0.5}\text{V}_{0.5}\text{O}_4:\text{Tm}^{3+}$ particles at different calcination temperatures. Obviously, with an increase of firing temperature, the characteristic diffraction peaks of

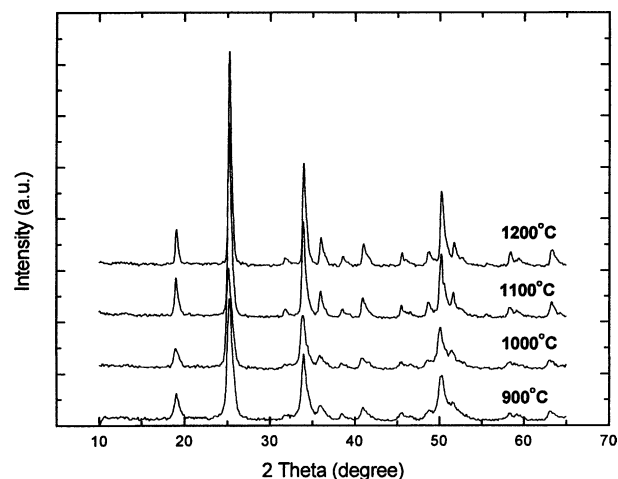


Fig. 1. XRD patterns of $(\text{Y,Gd})\text{P}_{0.5}\text{V}_{0.5}\text{O}_4:\text{Tm}^{3+}$ samples at different post-treatment temperatures.

$(\text{Y,Gd})\text{P}_{0.5}\text{V}_{0.5}\text{O}_4$ appeared. Up to 1200 °C, the enhanced diffraction peaks are observed, indicating full crystallization of $(\text{Y,Gd})\text{P}_{0.5}\text{V}_{0.5}\text{O}_4:\text{Tm}^{3+}$ particles.

Fig. 2 shows the SEM image of post-treated $(\text{Y,Gd})\text{P}_{0.5}\text{V}_{0.5}\text{O}_4:\text{Tm}^{3+}$ phosphor particles at 1200 °C for 2 h. It can be found that the size of the phosphor particles is uniform and submicron, and the morphology is regular, no agglomeration found. In practical application the morphology and size of particles greatly affect the properties of the phosphor materials. Phosphors with regular morphology and fine size can improve the packing density, slurry properties, and make the luminescence intensity uniform [16]. From this point of view, we believe that coprecipitation reaction is, at least for $(\text{Y,Gd})\text{P}_{0.5}\text{V}_{0.5}\text{O}_4:\text{Tm}^{3+}$ system, a doable preparation method for producing phosphors.

Fig. 3 shows the effect of post-treatment temperature on the luminescent intensity of phosphor $(\text{Y,Gd})\text{P}_{0.5}\text{V}_{0.5}\text{O}_4:\text{Tm}^{3+}$ under VUV (147 nm) excitation. The phosphor particles post-treated at 800 °C emitted little visible light.

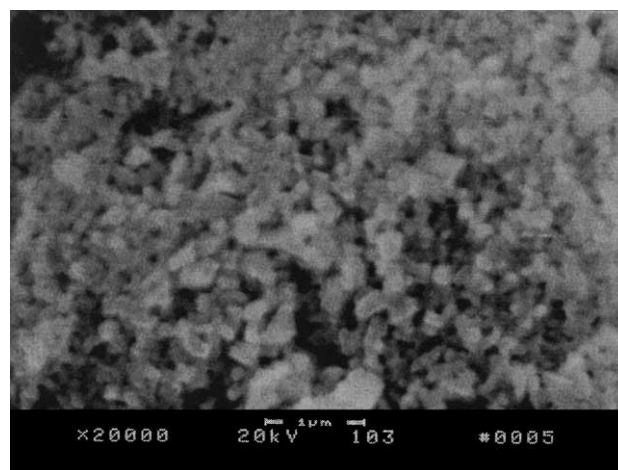


Fig. 2. SEM image of $(\text{Y,Gd})\text{P}_{0.5}\text{V}_{0.5}\text{O}_4:\text{Tm}^{3+}$ prepared by coprecipitation reaction (post-treated at 1200 °C for 2 h).

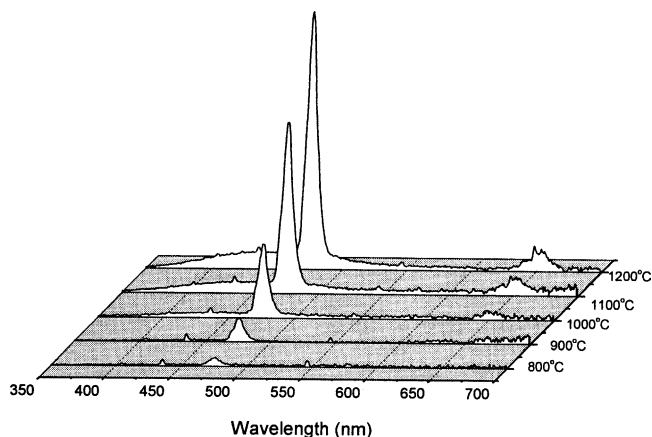


Fig. 3. The effect of post treatment temperature on the luminescent intensity of phosphor under 147 nm excitation.

With an increase of the post-treatment temperature, the luminescent intensities of the phosphor improved gradually. A weak peak around 650 nm attributes to Tm^{3+} ion transition $^1\text{G}_4 \rightarrow ^3\text{H}_4$.

The photoluminescence intensity of the phosphor of $(\text{Y,Gd})\text{P}_{0.5}\text{V}_{0.5}\text{O}_4:\text{Tm}^{3+}$ is affected by the post-treatment temperature, Tm^{3+} concentration, and mean size of particles. Fig. 4 shows the dependence of the luminous intensity of phosphor $(\text{Y,Gd})_{1-x}\text{Tm}_x\text{P}_{0.5}\text{V}_{0.5}\text{O}_4$ on the Tm^{3+} concentration under UV (254 nm) excitation. There are two emission peaks for most phosphors observed, the narrow one at 475 nm originates from the Tm^{3+} ion transition $^1\text{G}_4 \rightarrow ^3\text{H}_6$, and the weak broad-band around 430 nm belongs to VO_4^{3-} group. With increasing Tm^{3+} concentration, the narrow peak intensity enhanced while the Tm^{3+} concentration is lower than 0.0025 in mole. When the Tm^{3+} concentration is higher than 0.0025, the intensity of the transition $^1\text{G}_4 \rightarrow ^3\text{H}_6$ decreases with increasing Tm^{3+} concentration. The intensity of broad-band decreases with Tm^{3+} concentration in full studied

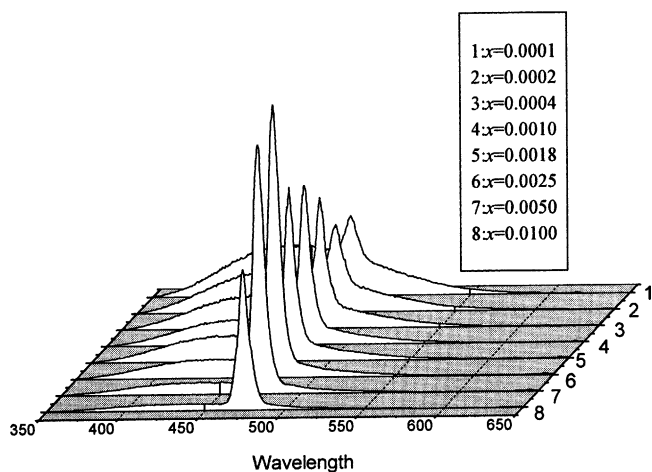


Fig. 4. Concentration dependence of integrated emission intensity of transition $^1\text{G}_4 \rightarrow ^3\text{H}_6$ of $(\text{Y,Gd})_{1-x}\text{Tm}_x\text{P}_{0.5}\text{V}_{0.5}\text{O}_4$ ($0.0001 \leq x \leq 0.010$) under 254 nm excitation.

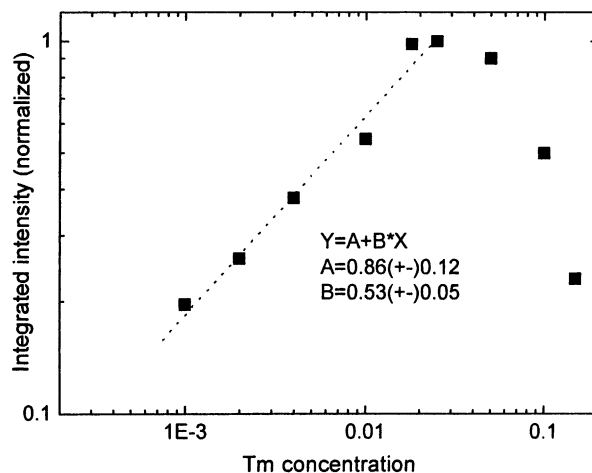


Fig. 5. Photoluminescence spectra of $(\text{Y,Gd})\text{P}_{0.5}\text{V}_{0.5}\text{O}_4:\text{Tm}^{3+}$ phosphor post-treated at different temperature under VUV (147 nm) excitation.

concentration region. The dependence of the transition intensity for $^1\text{G}_4 \rightarrow ^3\text{H}_6$ on Tm^{3+} concentration, represented in a double-log coordinates, is shown in Fig. 5. The integrated emission intensity is for the pure transition $^1\text{G}_4 \rightarrow ^3\text{H}_6$ of Tm^{3+} , which is obtained via multi-peak fit.

A linear fit of the experimental data in the Tm^{3+} concentration range between 0.0001 and 0.025 to the function, $Y=A+BX$, was carried out. The fitting results are shown in Fig. 5. From the fitting result, $B < 1$, it can be confirmed that there exists energy transfer from $^1\text{G}_4$ of Tm^{3+} to some quenching centers. The intensity decrease of VO_4^{3-} emission spectra with Tm^{3+} concentration implies the energy transfer from VO_4^{3-} to Tm^{3+} and its rate is smaller than that from Tm^{3+} to the quenching centers. This is the reason resulting in the extreme concentration quenching of Tm^{3+} in accordance with the experimental observation in Fig. 5.

4. Conclusions

Blue-emitting $(\text{Y,Gd})\text{P}_{0.5}\text{V}_{0.5}\text{O}_4:\text{Tm}^{3+}$ phosphor particles were prepared by coprecipitation reaction with a post-treatment process. The obtained particles have regular morphology with submicron size even after post-treated at 1200 °C for 2 h. The phosphor has an emission peak at 475 nm which is attributed to the emission from $^1\text{G}_4$ to $^3\text{H}_6$. It is expected that $(\text{Y,Gd})\text{P}_{0.5}\text{V}_{0.5}\text{O}_4:\text{Tm}^{3+}$ would be a promising blue-emitting candidate for PDP or specific detector phosphor.

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