

A New Sol–Gel Route to Synthesize YPO₄:Tb as a Green-emitting Phosphor for the Plasma Display Panels

Weihua Di,* Xiaojun Wang, Baojiu Chen, and Xiaoxia Zhao

Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and physics, Chinese Academy of Sciences, Changchun, 130033, P. R. China

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This work adopts a novel and low-cost sol–gel route to synthesize Tb³⁺-doped YPO₄ as a green-emitting phosphor for the plasma display panel (PDP). The phosphor obtained by this route shows improved luminescence efficiency in vacuum ultraviolet (VUV) excitation, compared with that obtained by a solid-state reaction.

Recently, the research in the vacuum ultraviolet (VUV) region has become a challenge in the field of luminescence of rare earth ions because of the development of phosphors used in the plasma display panel (PDP).^{1,2} The host for PDP phosphors is required to have band-gap absorption in VUV region.³ The phosphates are suggested to be a suitable host for PDP phosphors owing to high VUV absorption. Tb³⁺-activated YPO₄ and LaPO₄ are typical examples that are used as green-emitting PDP phosphors.^{4,5} The luminescent performance of PDP phosphors depends strongly on the synthetic route and procedure. In the case of synthesis of YPO₄:Tb, a solid-state reaction is usually used. However, this method has several disadvantages such as high-temperature process, long-time calcination and repeated milling and grinding. Accordingly, the phosphor particles by the solid-state reaction possess a large size, irregular shape, and coarse surface. In contrast, the wet chemical route may overcome these disadvantages mentioned above.^{6,7} Furthermore, the phosphor particles by the wet chemical route commonly have high composition homogeneity and phase purity. However, few report has been made for the synthesis of YPO₄ by sol–gel method, the only one even involved the use of metal alkoxides,⁸ which are very expensive and pollutive. This work aims at reporting a novel and low-cost sol–gel route to synthesize Tb-activated YPO₄. The luminescent characteristic of YPO₄:Tb from different synthetic routes under VUV excitation is compared.

Appropriate amount of Y₂O₃ (4N) and 1% mol Tb₄O₇ (4N) were dissolved in concentrated nitric acid to form Y(NO₃)₃ and Tb(NO₃)₃ solutions. These solutions were then passed through an OH⁻ exchange column with Dowex 1 × 4 (50–100 mesh) resin at room temperature. The flow of the solution was controlled to maintain the pH of the collected solution to be 11.0. Thus, the clear sols of Y(OH)₃ and Tb(OH)₃ were obtained. Trimethyl phosphate and ethanol were mixed in 1:10 ratio to get trimethyl phosphate stock solution. The stoichiometric amount of Y(OH)₃, Tb(OH)₃, and trimethyl phosphate solution, together with a small amount of boric acid as a flux were transferred to a round bottom flask, and peptized at 80 °C for 5 h in a stirrer. After the peptization, sol/gels were left in a container for 24 to 48 h until they became a thick gel, which was dried at 80 °C in an oven. After drying, the gel powder underwent two-step heat treatments at 300 and 1000 °C, respectively for 2 h in a reducing atmosphere

of N₂/H₂ to prevent the oxidation of Tb³⁺.

All the measurements were performed at room temperature. XRD studies were conducted on a Rigaku D/max-2000 X-ray powder diffractometer using Cu Kα radiation. SEM images were taken on a KYKY-1000 scanning electron microscopy. The excitation spectra were measured by using a vacuum ultraviolet monochromator and a deuterium (D₂) lamp and were normalized to that of sodium salicylate. The emission spectra were obtained under 147-nm excitation.

Figure 1 presents XRD patterns of YPO₄:Tb from sol–gel route annealed at 1000 °C. It is seen that all the diffraction peaks are well indexed to tetragonal xenotime structure of YPO₄ (JCPDS File No. 84-0335), indicating the formation of YPO₄ phase. The XRD data (not shown here) of the sample obtained from a solid-state reaction and calcinated at 1200 °C shows all the diffraction lines with almost the same intensity as observed in the sample from sol–gel route. This indicates the crystallization temperature for sol–gel route is 200 °C lower than that for a solid-state reaction. This is due to the fact that the precursor powders obtained from sol–gel route have very small size, and thus large surface area. This low-temperature synthesis not only prevents the introduction of the impurity, but controls the growth of phosphor particles effectively.

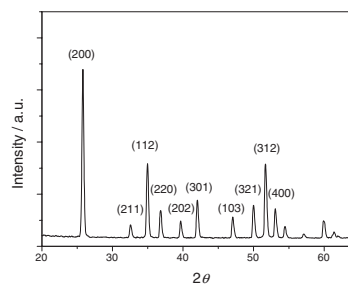


Figure 1. X-ray diffraction pattern of YPO₄:Tb obtained from sol–gel route and annealed at 1000 °C.

Figure 2 shows the morphology of YPO₄:Tb particle synthesized by sol–gel route and solid-state reactions, respectively. The YPO₄:Tb particle from sol–gel route possesses almost spherical shape, small size and smooth surface. In contrast, the irregular shape, large size, and poor surface quality are observed for the YPO₄:Tb particle from solid-state reactions. This morphological difference originates from different synthetic route. As is known, all of the starting materials are mixed at the molecular level in sol–gel route. In addition, a lower processing temperature is required and no milling and grinding processes are introduced. Thus the superior morphology of phosphor particles is observed, as shown in Figure 2a.

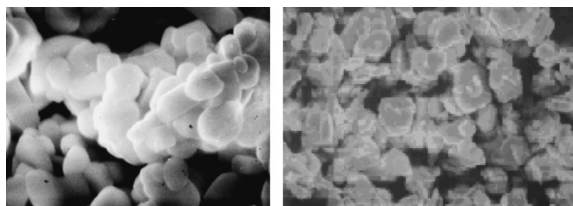
(a) --- 2 μm (b) --- 6 μm

Figure 2. SEM images of $\text{YPO}_4\text{:Tb}$ obtained by sol-gel route (a) and solid-state reaction (b).

It is well known that the luminescent performance of PDP phosphors depends strongly on the shape, size, surface, and dopant dispersity.^{9,10} Figure 3 presents the emission spectra of $\text{YPO}_4\text{:Tb}$ from sol-gel route and solid-state reaction in 147-nm excitation. The spectrum consists of lines ranging from 480 to 630 nm, which originate from the transitions between different f-electron states of Tb^{3+} , i.e., between the excited $^5\text{D}_4$ to the $^7\text{F}_j$ ($j = 6, 5, 4, 3$) ground states. The most intense emission is the $^5\text{D}_4$ to $^7\text{F}_5$ transition peaking around 543 nm, corresponding to the green emission. It is worth noting that the emission intensity of $\text{YPO}_4\text{:Tb}$ from sol-gel route is about 1.5 times higher than that from solid-state reactions. The luminescent efficiency of a phosphor is closely related to the host matrix purity and dopant homogeneity. Since the molecular-level reaction is achieved in sol-gel route, the doping of activators through solutions is straightforward, efficient, and highly homogeneous. Therefore, the homogeneous dispersion of dopant ions lowers the probability of ion interactions, thus enhancing the luminescent efficiency. Furthermore, as we have known, under VUV excitation, the energy is absorbed first by the host, and then transferred to the activators.¹¹ Therefore, the luminescence efficiency under VUV excitation depends strongly on the host absorption efficiency. However, VUV radiation only penetrates into a thin surface layer of phosphor particle within several tens nanometers, thus, the luminance of phosphors in VUV excitation largely comes from the surface contribution.^{3,11} Therefore, the surface quality of phosphor particles is a key factor to determine the luminescent efficiency. As observed in Figure 2a, the $\text{YPO}_4\text{:Tb}$ particles synthesized by sol-gel route have smooth surface and almost spherical shape. Such morphology may effectively decrease the scattering of incident light, thus enhancing the absorption to VUV radiation. In order to confirm this, the excitation spectra are shown in Figure 4. The spectrum consists of a few broad bands ranging from 140 to 280 nm. The band peaking around 150 nm should be ascribed to the host absorption. Other bands in the excitation spectrum are ascribed to the transitions from the lower energy level of the $4f^8$ configuration to the energy levels of the $4f^75d$ configuration of the Tb^{3+} . It is noted that the intensity of host absorption band of YPO_4 from sol-gel route is stronger than that from a solid-state reaction. This indicates that the efficiency of host absorption to VUV light is related to the synthetic route. The smooth surface and almost spherical shape of phosphor particles synthesized by sol-gel route contribute to

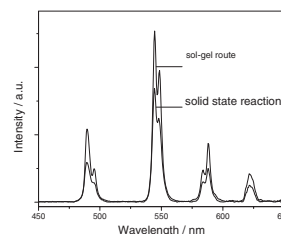


Figure 3. The emission spectra of $\text{YPO}_4\text{:Tb}$ from two different synthetic routes in 147-nm excitation.

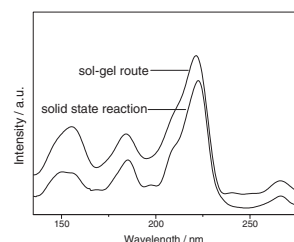


Figure 4. VUV-UV excitation spectrum of $\text{YPO}_4\text{:Tb}$ in 140–280-nm range by monitoring the $^5\text{D}_4$ to $^7\text{F}_5$ transition.

the host absorption to VUV light. Therefore, the luminescent efficiency in VUV excitation is improved by sol-gel route.

In conclusion, a novel and low-cost sol-gel route is used to synthesize Tb^{3+} -doped YPO_4 . High phase purity and dopant homogeneity, and superior particle morphology can be achieved by this route, thus improving the luminescent efficiency of $\text{YPO}_4\text{:Tb}$ as a PDP phosphor.

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