Preparation, characterization and VUV luminescence property of YPO$_4$:Tb phosphor for a PDP

Weihua Di *, Xiaojun Wang, Baojiu Chen, Huasheng Lai, Xiaoxia Zhao

Key Lab of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China

Received 17 July 2004; accepted 4 October 2004
Available online 6 November 2004

Abstract

Green-emitting phosphor YPO$_4$:Tb used in a PDP was prepared by two different methods, i.e., conventional solid-state reaction route and solution-based co-precipitation route. Results indicated that in solution-based co-precipitation route, a lower temperature was required, no grinding and milling processes were introduced, and the starting materials were mixed at molecular level, compared with conventional solid-state reaction route. Therefore, the phosphor particles obtained from solution-based co-precipitation route had several advantages in the morphology, such as excellent surface quality, almost spherical shape, narrow size distribution, and homogeneous composition. The excitation spectrum measurement showed that YPO$_4$ hosts had high energy absorption in VUV range, which makes it possible that YPO$_4$:Tb phosphors are used in a PDP. The emission spectrum of YPO$_4$:Tb under 147nm excitation indicated that the phosphor powders obtained from solution-based co-precipitation route had high luminance since they have excellent morphologies and homogeneous composition, compared with those obtained from conventional solid-state reaction route. © 2004 Elsevier B.V. All rights reserved.

Keywords: Co-precipitation; YPO$_4$; VUV; Luminescent properties

1. Introduction

Recently, the research on phosphors excited by vacuum ultraviolet (VUV) radiation has attracted considerable attention because they are newly applied in plasma display panels (PDPs) [1–3]. VUV is generally generated by the discharge of Xe/Ne gas [4], and it excites three color-based phosphors to produce the visible light. In order to understand VUV luminescence mechanism well, the researchers have devoted themselves to the studies on VUV luminescence properties in the recent several years [1,4]. LnPO$_4$ (Ln = Y, La, Gd, Lu) has high thermal and chemical stability [5] because these mentioned Ln$^{3+}$ has empty or half-filled or fully filled 4f electron shell with stable structure. LnPO$_4$ (Ln = Y, La, Gd, Lu) is suggested to be an excellent host for luminescent materials. For example, LaPO$_4$:Ce, Tb [6,7] has high luminescence efficiency in ultraviolet (UV) excitation and is used as a commercially used lamp phosphor up to now. Recent studies indicated that LnPO$_4$-based phosphors have high absorption in VUV range and show high luminescent efficiency under VUV excitation [4,8]. Therefore, LnPO$_4$-based phosphors are expected to be promising materials for PDP applications. Despite all that, little investigation has been conducted in the VUV optical properties of lanthanide phosphates and much previous work was focused mainly on their luminescent properties in UV region [6,7].

Commonly, the phosphor powders are prepared by conventional solid-state reaction at high temperature [9,10]. Although simply operated, this method has
several disadvantages including high-temperature processing, long calcination time and repeated milling and grinding.

High calcination temperature for long time can make the phosphor particles easily agglomerated to form a particle block, therefore, milling and grinding are required to achieve desirable particle size [11]. However, the surface of phosphors suffers from a damage in milling and grinding processes. Recent studies indicated that the penetration depth of VUV is about 100–200 nm [12], consequently, the surface damage resulting from grinding and milling processes will significantly degrade the luminescence properties of phosphors. Furthermore, due to the limitation of solid-state route, the resulting product prepared by this method is very difficult to achieve compositional homogeneity, and the doped ions are not able to be uniformly dispersed in the crystal lattice, thus, several impurities are more likely to be introduced and the luminescence efficiency is lowered.

For these disadvantages of solid-state method, several solution-based synthesis techniques, such as sol-gel [13] co-precipitation [14], spray pyrolysis [15], and hydrothermal method [16,17], have been developed. Since the starting materials are reacted at high level in solution-based synthesis, the resulting products exhibit better purity and high-degree compositional homogeneity. In this work, the solution-based co-precipitation method is applied to preparation of YPO₄:Tb phosphor powders. The phase structure and morphology are characterized respectively by X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements. The difference in the morphology of phosphor particles obtained by solid-state and solution-based methods is explained. The VUV luminescent property of YPO₄:Tb phosphor is determined, and the correlation of the luminescent intensity with the particle morphology is also investigated.

2. Experimental

Preparation of YPO₄:Tb by solid-state reaction: Ultra pure lanthanide oxide including Y₂O₃ (4N) and Tb₄O₇ (4N), and (NH₄)₂HPO₄, together with a small amount of Li₃PO₄ as a flux are used as the starting materials. These starting materials were finely ground in an agate mortar and then underwent the first firing at 850 °C for 2h in air. The mixture obtained from the first firing was subsequently ground again, and then underwent the second firing at 1200 °C for 2h in a reducing atmosphere.

Preparation of YPO₄ by co-precipitation method: Y₂O₃ and Tb₂O₇ were dissolved in concentrated nitric acid to form 0.5 M solution, together with which, the (NH₄)₂HPO₄ solution of same mol concentration was dripped into a vessel at a same speed to form white precipitate. The precipitate obtained was filtered and washed for three times with distilled water, then dried at 80 °C. The dried precipitate was mixed with a small amount of flux, and then fired at 1000 °C for 2h.

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.

3. Results and discussion

3.1. Structure characterization

YPO₄ phase has tetragonal xenotime structure [18] with space group of L₄₁/amd, [141]. The XRD pattern of Tb-doped YPO₄ obtained in this work show a slight shift of diffraction peaks, compared with that of the non-doped YPO₄ given in No. 84-0335 of JCPDS data files. This indicates that Tb³⁺ ions are successfully doped into the YPO₄ host, since a large difference in the radius of Y³⁺ and Tb³⁺ exists.

Fig. 1 shows the XRD patterns of YPO₄:Tb Powders prepared by solution-based co-precipitation and conventional solid-state routes. It can be seen that several characteristic diffraction peaks appear in the initial precipitate YPO₄:Tb, as shown in Fig. 1(a), although they have weak and broad diffraction line, which indicates that microcrystalline YPO₄ phase and no secondary

![Fig. 1. XRD patterns of YPO₄:Tb Powders prepared by solid state and co-precipitation routes. (a) the as-prepared precipitate obtained by co-precipitation; (b) the precipitate after 2h of calcination at 950°C (without flux); (c) the precipitate after 2h of calcination at 1100°C (without flux); (d) the precipitate after 2h of calcination at 1000°C (with flux); (e) the powder obtained from solid-state route (at 1200°C and with the same flux as (d)).](image-url)
phase have been formed in the initial precipitate. This is due to the fact that the starting materials in the solution-based co-precipitation are mixed at molecular level, thus improving the solubility and homogeneity of ions. Fig. 1(b) and (c) show XRD patterns of precipitates after 2 h of calcination respectively at 950 and 1100 °C without the addition of flux. With an increase of calcination temperature, intensifying and narrowing diffraction lines are observed, this indicates crystallite growth of YPO{sub 4} phase. It is observed that the XRD patterns in Fig. 1(a)–(c) shows broad diffraction peaks, so that YPO{sub 4}:Tb particles with nanometer size are expected to form. In the case of the nanoparticles, the mean particle size can be roughly determined from the broadening of the peak by using the Scherer formula. By fitting various peaks to this formula, we obtained the size of YPO{sub 4}:Tb particle in the range of 20–80 nm. This shows that the co-precipitation technique seems to be a useful way to prepare nano-sized YPO{sub 4} materials with high crystallinity, as shown in Fig. 1(c). In order to obtain bulk materials, flux is used. Fig. 1(d) shows the XRD pattern of YPO{sub 4}:Tb precipitate after 2 h of calcination at 1000 °C with the addition of flux, the increased peak intensity and narrowing peak width are observed, compared with in Fig. 1(c). This indicates that the flux is helpful to the growth of YPO{sub 4} crystal and that large-sized YPO{sub 4}:Tb particles are obtained by the addition of flux. The particle size is in micron size range obtained by SEM characterization, which is shown in the next section. For comparison, Fig. 1(e) shows the XRD pattern of YPO{sub 4}:Tb powders prepared by conventional solid-state reaction. It can be seen that the diffraction peaks of YPO{sub 4} powder obtained by co-precipitation technique at 1000 °C post-treatment have almost equal intensity as those of YPO{sub 4} powder obtained by conventional solid-state route at the calcination temperature of 1200 °C. It is concluded that the calcination temperature required by co-precipitation technique is about 200 °C lower than that required by conventional solid-state route. The reason for the decrease of calcination temperature required by co-precipitation technique probably comes from the two aspects as follows. On the one hand, the microcrystallite with a certain degree of crystallinity have been formed in the initial precipitate obtained by co-precipitation technique, as a result, a lower calcination temperature is required to achieve a high degree of crystallinity. On the other hand, it is observed from Fig. 1(a) the initial precipitate obtained by co-precipitation technique has a very small particle size, which means a large aspect surface. Thus, sufficient reaction can be achieved, which results in the decrease of calcination temperature.

### 3.2. Morphology characterization

The morphologies of YPO{sub 4}:Tb powders prepared by conventional solid-state route and co-precipitation technique are shown in Fig. 2(a) and (b), respectively. The YPO{sub 4}:Tb particles prepared by conventional solid-state route have an irregular shape, coarse surface, wide size distribution, and are highly aggregated, whereas the YPO{sub 4}:Tb particles prepared by co-precipitation technique have almost spherical shape, smooth surface, narrow size distribution in 1–2 μm range, and are loosely aggregated. The morphology difference above mentioned should originate from different preparation conditions and post-treatment techniques. In conventional solid-state reaction route, a high-temperature calcination is required for obtaining the phosphor materials with high crystallinity, however, high-temperature calcination makes the phosphor particles large and easily agglomerated, thus, milling and grinding appear necessary to obtain suitable particle size for application, but these post-treatment techniques significantly damage the surface quality of phosphor particles [19], as shown in Fig. 2(a). Compared with solid-state reaction route, the solution-based co-precipitation route needs a lower calcination temperature for the host crystallization and no milling and grinding processes. The growth of individual phosphor particles is effectively controlled with low calcination temperature, and the smooth surface is obtained due to without milling and grinding processes. Except for those, molecular-level mixture in solution-based co-precipitation makes the reaction highly homogeneous, which results in the formation of YPO{sub 4}:Tb particles with narrow size distribution. In conclusion, the use of solution-based co-precipitation technique markedly improves the morphology of phosphor particles, as shown in Fig. 2(b).

---

![Fig. 2. SEM patterns of YPO{sub 4}:Tb phosphor particle prepared by solid-state (a) and co-precipitation (b) routes.](image-url)

---

It is known that the morphology of phosphor particles plays an important role in improving the performance of flat panel displays. The phosphor particles with spherical shape are able to increase the screen brightness and improve the resolution [20] because of lower scattering of evolved light and higher packing densities than irregularly shaped particles obtained by conventional solid-state route. Furthermore, recent studies revealed that the VUV energy is absorbed in a very thin layer at the surface of the phosphor particles [12,21], so the surface quality of phosphor particles seems to be very important for the luminescent efficiency. Milling and grinding processes are introduced in the phosphor prepared by conventional solid-state route, thus, the surface quality of phosphor is degraded, which is expected to influence the absorption of VUV energy significantly. As shown in Fig. 2(b), the phosphor particles obtained from co-precipitation route have excellent morphology and homogeneous size distribution, therefore, it is predicted that the phosphor particles obtained from co-precipitation route have higher luminance than those obtained from conventional solid-state reaction, which is discussed in the following section.

3.3. VUV luminescence property

Fig. 3 shows the emission spectra of Tb doped YPO$_4$ under 147 nm excitation. The emissions from Tb doped YPO$_4$ mainly result from the transitions of $^5$D$_3$ and $^7$F$_j$ (where $j = 1, \ldots, 6$, the 7f ground state is split into seven levels by spin–orbit coupling). The spectral energy distribution of Tb$^{3+}$ emission depends strongly on Tb concentration. At a very low concentration of Tb, the emission from $^5$D$_3$ to $^7$F$_j$ level is observed obviously, as shown in Fig. 3(a); with an increase of Tb concentration, the emissions from $^5$D$_3$ to $^7$F$_j$ level are quenched gradually by the cross relaxation process, as described in formula 1. This cross relaxation process produces rapid population of the $^5$D$_4$ level at the expense of $^5$D$_3$, resulting in a strong emission from $^5$D$_4$ to $^7$F$_j$ level, as shown in Fig. 3(b). The Tb$^{3+}$ emission features observed under VUV excitation is similar to that observed under UV excitation [4].

\[
\text{Tb}^{3+}(^5\text{D}_3) + \text{Tb}^{3+}(^7\text{F}_0) \rightarrow \text{Tb}^{3+}(^5\text{D}_4) + \text{Tb}^{3+}(^7\text{F}_0)
\]  

Fig. 4 shows the excitation spectrum by monitoring the $^5$D$_4$–$^7$F$_5$ emission in the Tb doped YPO$_4$. The excitation spectrum consists of several broad bands. According to different excitation mechanism, we divide these bands into two parts, one in the region from 125 to 160 nm, the other from 160 to 300 nm. The latter are assigned to the transitions from the lower energy level of the 4f$^8$ configuration to the energy levels of the 4f$^7$5d configuration of the Tb$^{3+}$, resulting in a direct excitation into Tb$^{3+}$. The former should be assigned to the host absorption, since it is indicated in K.S. Sohn report [22] that the excitation energy at 160 nm is the absorption edge of the YPO$_4$ host. Therefore, when Tb doped YPO$_4$ is excited at wavelengths shorter than 160 nm, the excitation is absorbed first by the host and then transferred to Tb$^{3+}$ ions, leading to an indirect excitation into Tb$^{3+}$. As a case, the luminescent efficiency of the Tb$^{3+}$ under the excitation at wavelength shorter than 160 nm depends strongly on the absorption efficiency of the host. As mentioned above, the phosphor powders obtained from solution-based route have higher luminance than those obtained from solid-state route, since they have higher absorption efficiency of energy due to their excellent morphology. According the excitation spectrum, the Tb doped YPO$_4$ phosphor exhibits a strong absorption in the VUV range, even if this absorption in the VUV range is not as strong as the highest 4f–5d transition band of the Tb$^{3+}$ in the UV range. Concerning improving the absorption in VUV range, more work is required.
Fig. 5 shows the comparison of luminescent intensity of 10mol% Tb doped YPO$_4$ obtained by these two different preparation routes, i.e., solid-state reaction and solution-based technique respectively. Clearly, the luminescent intensity of phosphor powders obtained from solution-based route is higher than that obtained from solid-state reaction route. Similarly, this result is also obtained in other concentrations of Tb doped YPO$_4$. As mentioned previously, the phosphor particles prepared by solution-based route have excellent surface quality and narrow size distribution, compared with those by solid-state route, consequently, the VUV energy is effectively absorbed at the surface of phosphor particles. This is one of the reasons that can explain the difference in the luminescent intensity of phosphor powders obtained from two different preparation routes. Furthermore, the starting materials in the solution-based reaction are mixed at the molecular level, so the doped ions are able to efficiently enter and be uniformly dispersed in the host lattice. Consequently, the resulting materials can achieve compositional homogeneity. However, the phosphor powders prepared by conventional solid-state route are very difficult to achieve this compositional homogeneity, it is inevitable for the formation of several impurities containing the doped ions, although they are difficultly detected by characterization method such as XRD due to a small amount. As a result, these impurities markedly degrade the luminescent intensity of phosphors.

4. Conclusions

Solid-state and solution-based reaction routes are used to synthesize the green-emitting phosphor for PDP applications. By comparison, advantages of solution-based reaction route are summarized as follows: lower calcinations temperature, excellent particle morphology, and higher compositional homogeneity.

YPO$_4$:Tb phosphors have strong excitation bands in VUV range, indicating high VUV energy absorption. The phosphors prepared by solution-based route have superior luminescence, since they have excellent particle morphology and high compositional homogeneity, compared with those prepared by solid-state reaction route.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 50172046, 50102006) and the State 863 Project (Grant No. 2002AA311160).

References