Synthesis of Agglomerate-Free YAG: Ce^{3+} Phosphors by Co-Precipitation and Low Temperature Spray Pyrolysis

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Abstract

$Y_{3-x}Ce_xAl_5O_{12}$ (YAG: Ce^{3+}) phosphor particles were prepared by a new method called co-precipitation and low temperature spray pyrolysis (CP-LTSP) with oxalic acid and ammonia as precipitant. It corresponds to the first-step chemical liquid reaction, the second step dehydration and partial decomposition of precipitation droplets at 250 °C and then heating at 1100 °C or above. Spherical as-prepared particles and agglomerate-free YAG: Ce^{3+} phosphor particles were obtained respectively. Pure YAG phase could be formed after LTSP at 250 °C and then annealing at 1100 °C for 4 h. The emission spectra and XRD patterns of YAG: Ce^{3+} phosphor particles indicated that the optimum doping concentration of Ce^{3+} was 0.06. The emission intensity increased with the increase of annealing temperature. As a result, the YAG: Ce^{3+} phosphor particles without optimization annealed at 1550 °C for 4 h had the similar emission intensity (96%) of the commercial phosphor by the solid-state method.

1. Introduction

Cerium-doped yttrium aluminum garnet ($Y_{3-x}Ce_xAl_5O_{12}$, YAG: Ce^{3+}) is a yellow light emitting phosphor with excitation in the blue region, i.e., to the highly efficient emission of blue InGaN/AlGaN chips. It has the great importance for application in white LEDs [1].

Solid-state method is the conventional synthetic route for preparing phosphor particles in large-scale production. However, this conventional process has disadvantages in maintaining the composition uniformity and avoiding agglomeration, which strongly affected the luminous characteristics of phosphor particles [2]. New methods for preparing YAG: Ce^{3+} phosphor has been studied, such as co-precipitation method [3], sol-gel [4], microemulsion method [5], and hydrothermal synthesis [6] et al. Though these methods have solved some problems, there are still some drawbacks. For example, co-precipitation method cannot solve the problem of agglomeration in the drying period. Comparatively speaking, the spray pyrolysis (SP) method is a feasible process to avoid agglomeration.

The SP method, which has been applied in the preparation of phosphor materials [2, 7-9], is recommended as a promising method for preparing particles with spherical shape, narrow size distribution, and agglomerate-free characteristic. In general, the phosphor particles prepared by SP are obtained from spray solution. In this paper, the co-precipitation process was first introduced as spray suspension to take the place of spray solution. Agglomerate-free YAG: Ce^{3+} phosphor particles were obtained via spray suspension under co-precipitation and low temperature spray pyrolysis (CP-LTSP), and the LTSP had been reported before [10, 11]. Thermal properties of as-prepared particles, effects of the doping concentration of Ce^{3+}, annealing temperature on morphology and the emission intensity of YAG: Ce^{3+} phosphor particles were investigated. Furthermore, the results were compared with the international mainstream commercial product.

2. Experimental

The spray equipment consists of a peristaltic pump, an atomizing disc (Ohkawara Co., model MC-50, SUS304/ZrO_2), a sus304 stainless reactor (length, 1200 mm and inner diameter, 800 mm) and a collector system. The inflow wind temperature was 250 °C.

The co-precipitate in spray suspension was prepared by chemical liquid reaction. Oxalic acid and ammonia was used as precipitant. To prepare the spray suspension, first, the metal salts solution was made by dissolving Y_2O_3 (99.99%), $Al(NO_3)_3{\cdot}9H_2O$ (99.99%), $Ce(NO_3)_3{\cdot}6H_2O$ (99.99%) into 500ml deionized water according to stoichiometric proportion of $Y_{3-x}Ce_xAl_5O_{12}$ (x =

2011 International Symposium on Advanced Packaging Materials (APM 2011)
978-1-4673-0149-7/11/$26.00 ©2011 IEEE

0.04, 0.06, 0.08, 0.10). The total cation concentration was 0.4 mol/L. Next, the precipitant solution was prepared by adding oxalic acid and ammonia into 1 L deionized water. Then, the metal salts solution was added at a speed of 6 ml/min into the precipitant solution under mild stirring at 70 °C. During the titration, certain amount of ammonia was added to keep the pH at 9~10. After titration, the suspension was aged for 24 h, then filtered and washed with alcohol. Finally, the spray suspension was prepared by adding the precipitate into 600 ml deionized water.

The prepared spray suspension was atomized at the rotation rate of 24000 r/min and formed droplets in the spray reactor. The as-prepared particles obtained by LTSP at 250 °C were annealed at 950-1550 °C for 4 h under reducing atmosphere.

The YAG: Ce^{3+} phosphor particles were characterized by different techniques, such as DTA/TG (Netzsch, STA409EP), XRD (Philips, Panalytical X'pert PRO), SEM (Philips, XL30 ESEM), and photoluminescence (Hitachi, F-4500).

3. Results and discussion

During the titration, the hydroxide and oxalic precipitate were formed in solution according to the eq. (1), (2) and (3) [12, 13]. Ammonia could furnish OH^- ions which can remove the H^+ in equation (1) and (2) to push the reactions. Finally, the $Al(OH)_3$ would be converted to γ-AlOOH according to eq. (4) at 200 °C [12] during LTSP. The $Y_2(C_2O_4)_3 \cdot xH_2O$ would be converted to $Y_2(C_2O_4)_3$ at 410°C and Y_2O_3 at 735°C respectively[13], according to equation (5) during the annealing process.

$$Al(NO_3)_3 + 3H_2O \leftrightarrow Al(OH)_3 + 3NO^-_3 + 3H^+ \quad (1)$$

$$2Y^{3+} + 3H_2C_2O_4 \leftrightarrow Y_2(C_2O_4)_3 \cdot xH_2O + 6H^+ \quad (2)$$

$$NH_3 \cdot H_2O \leftrightarrow NH^{4+} + OH^- \quad (3)$$

$$Al(OH)_3 \rightarrow \gamma\text{-}AlOOH + H_2O \quad (4)$$

$$Y_2(C_2O_4)_3 \cdot xH_2O \rightarrow Y_2(C_2O_4)_3 + xH_2O_3 \rightarrow Y_2O_3 \quad (5)$$

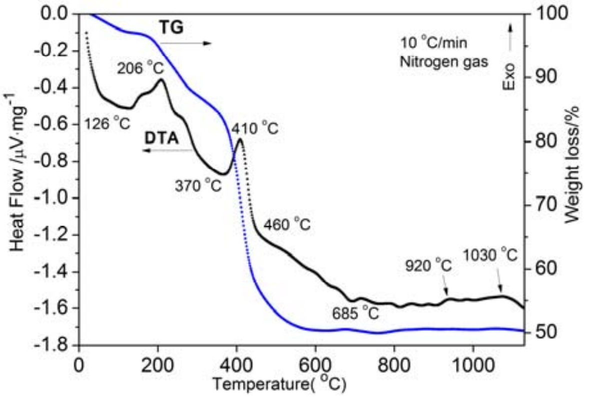

Fig.1 DTA/TG curves of YAG: Ce3+ precursor as-prepared by co-precipitation and low temperature spray pyrolysis (CP-LTSP)

DTA/TG curves of the YAG: Ce^{3+} precursor prepared by the CP-LTSP method are given in Fig. 1. The TG curve indicates an overall weight loss of approximately 48% and much of the loss takes place below 600 °C. The weight loss at lower temperatures is mainly due to the release of absorbed water, molecular water and the decomposition of oxalate, hydrate, corresponding to the DTA curve. Two exothermic peaks almost without weight loss at 950 °C and 1080 °C in the DTA curve which can be attributed to the crystalline of YAP and YAG phase respectively, as evidenced by the XRD results in Fig. 2a.

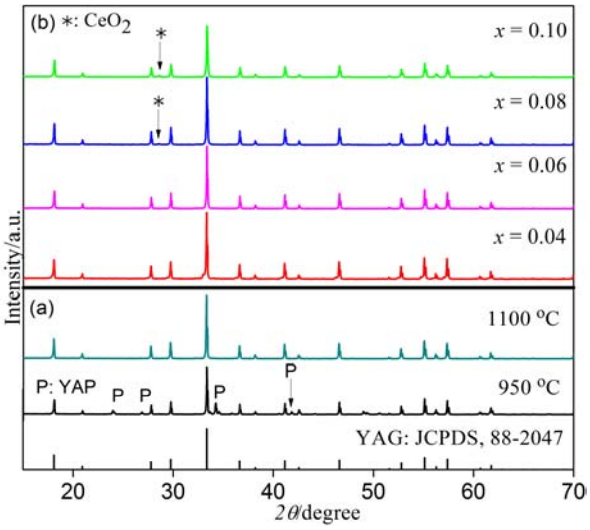

Fig. 2 XRD patterns of $Y_{3-x}Ce_xAl_5O_{12}$ at (a) heat-treated at different temperature for 4 h; (b) doped at different concentration of Ce^{3+}, and then heat-treated at 1550 °C for 4 h.

Fig. 2a shows the XRD patterns of YAG: Ce^{3+} precursor prepared by the CP-LTSP method after annealing at 950 °C and 1100 °C for 4 h respectively. YAG phase (JCPDS No. 88-2047) was crystallized at 950 °C with the presence of small peaks of YAP phase (JCPDS No. 70-1677). Pure YAG phase was obtained at 1100 °C. These results are consistent with the DTA/TG curves in Fig. 1.

In the YAG: Ce^{3+} phosphor, Ce^{3+} acts as the activator. The emission intensity is strongly impacted by the doping concentration of Ce^{3+} in the YAG host lattice. As reported by previous works [2, 3, 6, 14], the optimum doping concentration of Ce^{3+} was from 0.03 to 0.10 by different methods. In this paper, Ce^{3+} was added at x = 0.04, 0.06, 0.08 and 0.10 ($Y_{3-x}Ce_xAl_5O_{12}$) to find the optimum doping concentration for best luminescence.

Fig. 2b shows the XRD patterns of YAG: Ce^{3+} precursor annealed at 1550 °C for 4 h at different doping concentrations of Ce^{3+}. The samples obtained at x = 0.04 and 0.06 have pure YAG phase, but CeO_2 minority phase (symbol: *) when x = 0.08 and 0.10. The substitution of the bigger Ce^{3+} (R: 114 pm) with Y^{3+} (R: 102 pm) [7] would lead to the expansion of YAG lattice parameter. Therefore, an excess of the solubility limit is evident due to the detection of CeO_2 present as a minority phase when $x \geq 0.08$.

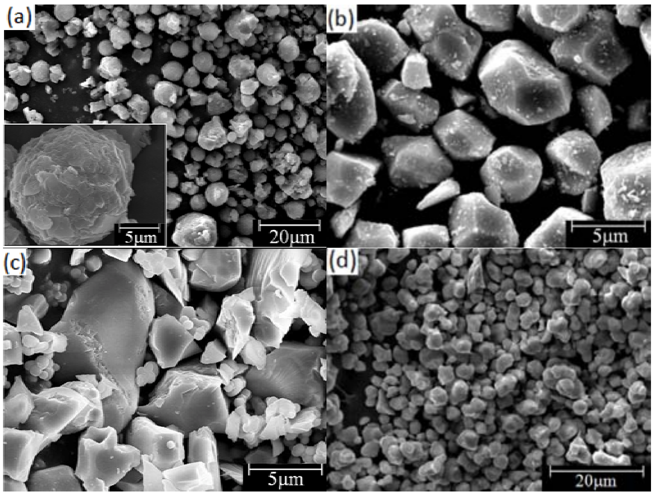

Fig. 3 Particle photographs of YAG: Ce^{3} SEM; (a) precursor prepared by CP-LTSP; (b), (d) particles prepared by CP-LTSP and then heat-treated at 1550 °C for 4h; (c) commercial powder HD432.

Fig. 3a shows the SEM image of spherical YAG: Ce^{3+} precursor particles directly prepared by CTSP. According to our research, the collection efficiency and mean size were strongly affected by the total cation concentration [15].

Fig. 3b shows the SEM image of YAG: Ce^{3+} phosphor particles annealed at 1550 °C for 4 h. The sphericity had disappeared and the morphology of the precursor particles had changed to hexagonal prism-like shape without agglomeration. YAG: Ce^{3+} precursor particles directly prepared by CP-LTSP were comprised of oxalic precipitation and hydroxide precipitation. During the heating period a great deal of gas was released, as evidenced by the DTA/TG curves in Fig. 1, which separated the particles that were close to each other and thus avoided agglomeration. From Fig. 3b we can clearly see that agglomerate-free YAG: Ce^{3+} phosphor particles with high crystalline (Fig. 2a) and high emission intensity (Fig. 4a) were synthesized at 1550 °C for 4 h.

For comparison, the international mainstream commercial product (Hung ta trading Co., Ltd., HD432) was characterized (Fig. 3c). The commercial product was prepared by conventional solid-state reaction method. The milling process in solid-state route produced fragments and damage to the crystal morphology, which degraded the emission intensity of phosphor. From Fig. 3b and Fig. 3c, it is clear that the CP-LTSP method could prepare agglomerate-free YAG: Ce^{3+} phosphor particles with narrow size distribution, less fragments produced by the milling process and intact crystal morphology. Therefore, the sphericity of precursor particles prepared by CP-LTSP is a desirable and promising morphology for phosphor annealing at high temperature.

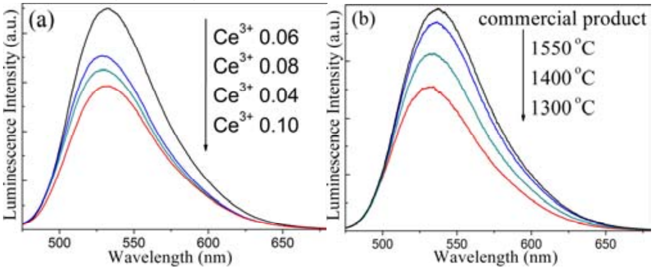

Fig. 4 Emission spectra of $Y_{3-x}Ce_xAl_5O_{12}$ phosphor (a) doped at different concentration of Ce^{3+}, and then heat-treated at 1550 °C for 4 h; (b) heat-treated at different temperature for 4 h, compared with commercial product HD432, under 460 nm excitation.

Fig. 4 is the emission spectra of YAG: Ce^{3+} phosphor prepared by the CP-LTSP method at different doping concentrations of Ce^{3+} and annealing temperatures, respectively. The YAG: Ce^{3+} phosphor was excited at 460 nm. The peaks of the emission spectra are at near 532 nm, which is characteristic of the strongest transition. In accordance to the literature [16], it is ascribed to the electron transition from the excited state of 5d level to the ground state Ce^{3+} ($^2F_{5/2}$, $^2F_{7/2}$).

It is observed from Fig. 4a that the maximum intensity was obtained at $x = 0.06$ and the intensity decreased with the increase of doping concentration of Ce^{3+} at $x = 0.08$ and 0.10. According to the doping mechanism [17], an increase in Ce^{3+} doping concentration might affect the rate of nonradiative decay via cross correlation caused by energy exchange between two neighboring activator ions and by the migration of the excitation from one ion to another one throughout the crystal. When $x = 0.04$, the Y^{3+} were partially substituted by Ce^{3+} in the YAG host lattice. However, an incomplete substitution could not reach the maximum intensity.

Fig. 4b shows the emission spectra of YAG: Ce^{3+} phosphor prepared by CP-CTSP increased monotonically with the increase of annealing temperature. The maximum intensity was obtained at the highest annealing temperature because of the optimum Ce^{3+} doping concentration and high crystalline of agglomeration-free phosphor particles. The emission intensity of commercial product was also shown in Fig. 4b. The emission intensity of YAG: Ce^{3+} phosphor prepared by CP-LTSP method at 1550 °C for 4 h, which was not optimized, reached 96% of commercial product (HD432).

As it is shown in Fig. 3c, the commercial product was comprised of fragments produced by the milling process, irregular morphology large particles (6-12 μm) and spherical morphology small particles (less than 1 μm). This combination, except the fragments, increased the packing density and expanded the effective light emitting area. However, the particle agglomeration and damage to the crystal morphology by the milling process which degraded the emission intensity.

Therefore, the emission intensity of agglomeration-free particles prepared by CP-LTSP method would be improved by mixing proper amount spherical small particles.

4. Conclusions

Agglomerate-free YAG: Ce^{3+} phosphor with high crystalline and high emission intensity was prepared by CP-LTSP method. It corresponded to the initial dehydration and then partial decomposition of so precipitated droplets up to 250 °C about 30mins to obtain spherical precursors, and then additional heat treatment at 1100 °C or above for 4 h.

The emission spectra and XRD patterns of YAG: Ce^{3+} phosphor indicate that the optimum doping-concentration of Ce^{3+} was obtained at x= 0.06 ($Y_{3-x}Ce_xAl_5O_{12}$). The emission intensity of YAG: Ce^{3+} becomes bigger with the increase of heat treatment temperature. The as prepared YAG: Ce^{3+} phosphor without optimization could reach 96% relative intensity of commercial phosphor prepared by conventional solid-state method.

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