

Preparation of YAG:Ce³⁺ phosphor by sol-gel low temperature combustion method and its luminescent properties

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Abstract: YAG:Ce³⁺ phosphor was prepared by sol-gel low-temperature combustion method. The effects of the precursor properties and calcining temperature on the crystallization process, microscopic morphology and luminescent properties of phosphor were studied. The results indicate that the pure phase of YAG can be obtained at 800 °C by sol-gel low temperature combustion method, using citric acid as complexing agent. When the molar ratio of metal ion to citric acid is 2.0 and pH value is 2, the crystallinity increases and the phosphor particle size grows up gradually with the increase of the calcining temperature. The powders were characterized through thermal analysis, X-ray diffraction analysis and scanning electron microscope analysis. The excitation spectra of YAG:Ce³⁺ phosphor take on a double peak structure, and the peak value of the main excitation spectra occurs at 460 nm and that of the emission spectra is near 530 nm. With the gradual increase of the calcining temperature, the peak position of excitation and emission spectra remains basically unchanged, but its relative intensity increases gradually.

Key words: YAG:Ce³⁺ phosphor; sol-gel; low-temperature combustion method; crystallization; microscopic morphology

1 Introduction

Yttrium aluminum garnet(YAG) has been widely used as matrix-materials of laser and luminescence[1–3] because of its excellent thermal conductivity, high mechanical strength, high temperature resistance and radiation resistance. Due to the special electronic structure of rare earth ions where the electrons on its 5d orbits are in an exposure condition without shielding, these electrons make a transition from 5d to 4f on the effect of external factors, and consequently activate the YAG[4]. BLASSE and BRIL[5] first prepared YAG:Ce³⁺ phosphor and studied its luminescence performance. And this phosphor has been successfully applied to the white light emitting devices(LED).

The methods to prepare YAG:Ce³⁺ phosphor mainly include solid-state reaction[6–10], co-precipitation [11–15], polymer network[16] and sol-gel process [17–18], etc. Among them, the high-temperature solid-state reaction method is normally used to produce YAG:Ce³⁺ phosphor in industry. Although a higher

luminescence intensity and luminance can be obtained by this method, it needs high reaction synthesis temperature and long reaction time, furthermore, the grain size of the phosphor has abnormal growth and has a wide size distribution, which often causes the phosphor to be ground twice. Therefore, the cost of productions is increased. The co-precipitation method is difficult to achieve industrialization. And the polymer network method is hard to remove the residual carbon in the powders, which results in the poor luminescence performance. Also some researchers prepared YAG:Ce³⁺ phosphor by sol-gel method with metal alkoxides as raw materials, but the process is not easy to control, the preparation flowsheet is long, and the moisture enwrapped in colloids is difficult to loose[19–21].

At present, few reports about preparing the YAG:Ce³⁺ phosphor can be seen using the sol-gel low temperature combustion method. To gain YAG:Ce³⁺ phosphor with high crystallinity, small grain size and uniform morphology at low preparation temperature is the purpose of this research. Sol-gel was firstly prepared by the complex method using rare earth oxides, inorganic

nitrate and citric acid as raw materials, and then YAG:Ce³⁺ phosphor by low-temperature reaction combustion was obtained.

2 Experimental

2.1 Raw materials

High-purity Y₂O₃ (99.995%, Shanghai Yuelong Chemical Ltd.) and the chemically pure reagents were mentioned as follows: nitric acid (HNO₃), Ce(NO₃)₃·6H₂O, Al(NO₃)₃·9H₂O, citric acid (C₆H₈O₇·H₂O), and ammonia (NH₃·H₂O).

2.2 Preparation of phosphor powder

The processing steps of low temperature combustion method are shown in Fig.1.

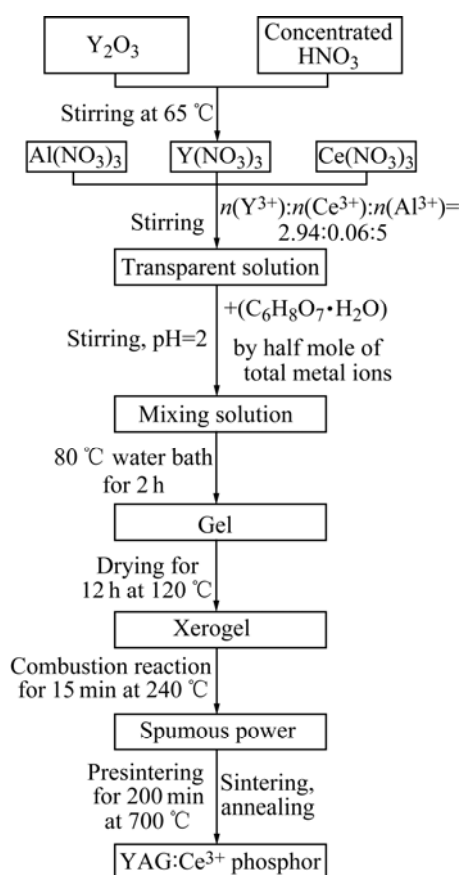


Fig.1 Flow chart of YAG:Ce³⁺ phosphor prepared by low temperature combustion method

Citric acid (C₆H₈O₇·H₂O) was dissolved in YAG transparent solution by half the mole of the total metal ions. The pH value of the solution was modulated to 2, and a gel was obtained for 2 h by immersing the solution in a water bath at 80 °C. Then the gels were dried to obtain canary xerogel, and the xerogel was put into a muffle stove and a combustion reaction occurred, then spumous powder was obtained. The calcination was

conducted at 700 °C with a heating rate of 2 °C/min and kept for 200 min, then the temperature was increased up to different holding temperatures (800–1 300 °C) at a rate of 10 °C/min for a fixed holding time of 300 min in air.

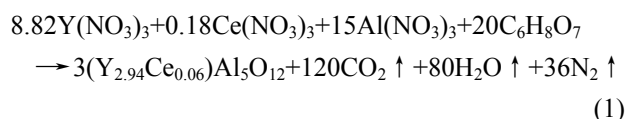
2.3 Characterization of phosphor powders

Phase analysis was accomplished with an X-ray diffractometer using Cu K_α radiation (X'Pert Pro, Philips, Netherlands). Micrographs were obtained by scanning electron microscopy (SEM, LEO 1530, Germany) under a working voltage of 40 kV and an electric current of 20 mA to observe the morphology and particle size of the sample. The luminescence spectra were taken on a spectrofluorometer (HITACHI F4500, Japan). The precursors were studied by thermo analysis method with a thermal analyzer (STA409EP, Netzsch, Germany).

3 Results and discussion

3.1 Thermal analysis of precursors

The combustion system is composed of nitrate as oxidant and citric acid as reductant. The relative ratio of the two compositions will impact the combustion procedure. The combustion reaction can be expressed by



From reaction (1), the molar ratio of metal ion to citric acid ($n(\text{M})/n(\text{C})$) can be found out to be 1.2. However, in practice, there is a deviation of 1.2 (the theoretical value) due to the decomposition of the citric acid and nitrate when being heated. In this work, we take the $n(\text{M})/n(\text{C})$ value as 2.0.

The DTA-TG curve of the precursor xerogel prepared by sol-gel low temperature combustion method under pH=2 is shown in Fig.2.

From Fig.2, it can be seen that most of the mass loss occurs below 600 °C, and the mass loss is about 69.83%, which is mainly due to the evaporation of the adsorbing water, and the decomposition of both the nitrate and the organic complex compound. Simultaneously, one endothermic peak and three exothermic peaks exist in DTA curve in the course of the mass loss. The endothermic peak occurs at 119 °C because of the evaporation of the adsorbing water on the xerogel surface. Therefore, in the course of the evaporation, the mass loss is fewer. Next, the DTA curve has three exothermic peaks, accompanied by remarkable mass loss. The first exothermic peak occurs at 202 °C, which results from the decomposing removal of nitrate in xerogel. The second peak around 295 °C is ascribed to

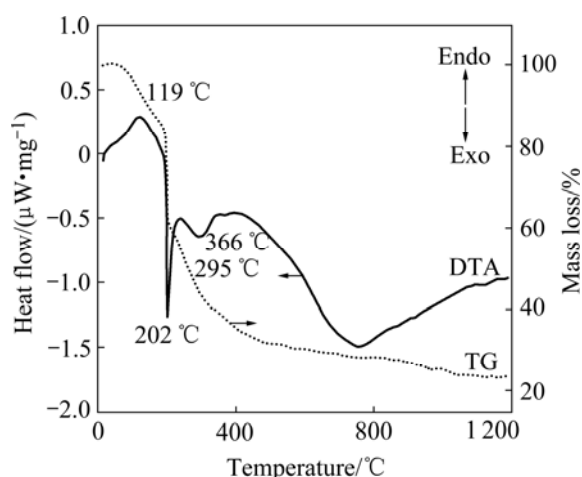


Fig.2 DTA-TG curves of precursor xerogel (pH=2, $n(M)/n(C)=2.0$)

the reaction of residual nitrate with citric acid forming carbonate and the third peak around 366 °C is due to the decomposition of the carbonate. The TG curve has no remarkable change within the range of 600–1 000 °C, which means the mass loss is not very obvious. As shown in Fig.3, the YAG phase occurs from 700 °C to 800 °C, which indicates that the exothermic peak emerging around 759 °C on the DTA curve is caused by the formation of YAG crystal phase.

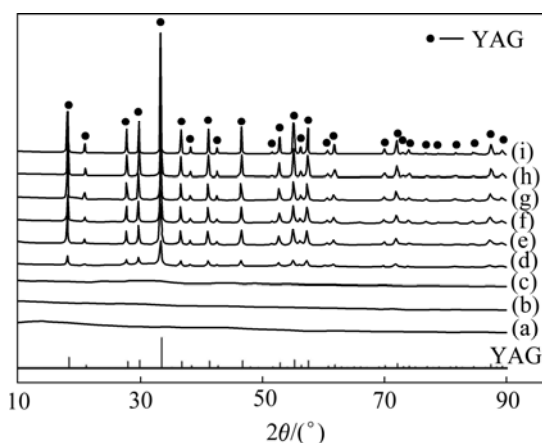


Fig.3 XRD patterns of sample at different temperatures: (a) Xerogel; (b) 240 °C; (c) 700 °C; (d) 800 °C; (e) 900 °C; (f) 1 000 °C; (g) 1 100 °C; (h) 1 200 °C; (i) 1 300 °C

3.2 Effects of calcining temperature on crystallization process and microstructure

XRD patterns of the precursors prepared by sol-gel low temperature combustion method and the products at different temperatures are shown in Fig.3.

The preparation conditions are as follows: citric acid is used as complexing agent, pH value is 2 and $n(M)/n(C)$ is equal to 2.0. As shown in Fig.3, the XRD

patterns of the xerogel precursors and the product obtained at 240 °C indicate that the sample is in amorphous and no obvious diffraction peak exists. After being presintered, it has a non-crystalline broad peak around 33.30° (2θ), which shows that it is amorphous powder. When the temperature increases to 800 °C, a more consummate YAG phase forms, and no other impurity phases exist. As the temperature increases, the crystallization is enhanced, and the diffraction peak intensity increases, which reveals that the powder grain grows gradually and YAG single phase remains unchanged, and no new phase or impurity phase is detected. The XRD pattern at 1 300 °C agrees with the standard PDF card of YAG (No.82-0575) very well. Compared with other synthesis methods, pure YAG phase can be obtained by sol-gel low temperature combustion method at a relative lower temperature of 800 °C, and no YAM, YAP or other impurity phase exists.

The curve of phosphor's average grain size varying with the temperature, which is calculated with Scherrer's formula, is shown in Fig.4.

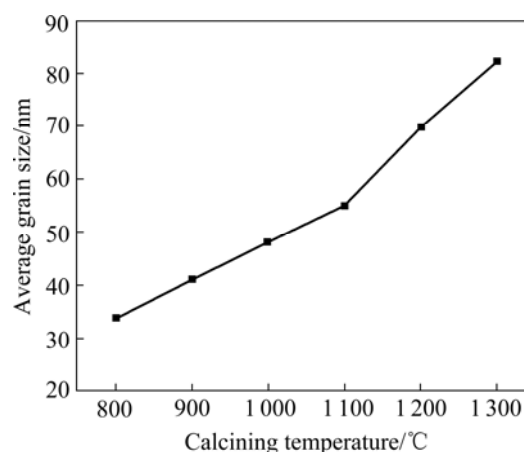


Fig.4 Average grain size of sample prepared by low temperature combustion method and calcined at different temperatures

From Fig.4, it can be seen that the average grain size of YAG:Ce³⁺ phosphor increases markedly with the elevation of the calcining temperature.

The SEM images of YAG phosphor at different calcining temperatures are shown in Fig.5.

It can be seen from Fig.5(a) that the particles of the powder are very fine and uniform, and the grain size is mostly 20–30 nm when being presintered at 700 °C. The particles with regular shape appear at 800 °C, but the particles accumulate closely as shown in Fig.5(b). The particles start to bond together and the size enlarges obviously upon being heated to 900 °C as shown in Fig.5(c), which is due to the grains, pore size and shape

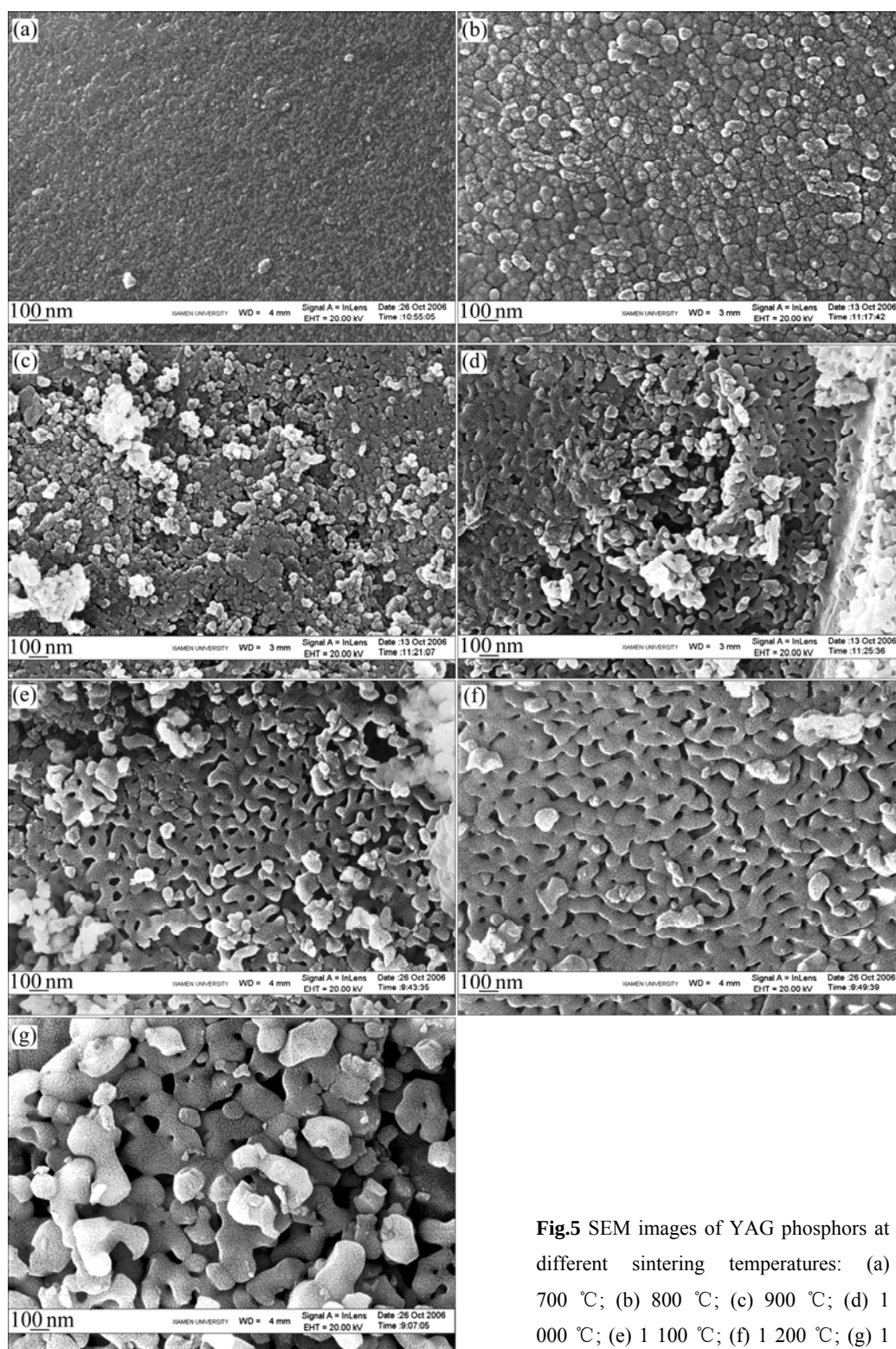


Fig.5 SEM images of YAG phosphors at different sintering temperatures: (a) 700 °C; (b) 800 °C; (c) 900 °C; (d) 1000 °C; (e) 1100 °C; (f) 1200 °C; (g) 1200 °C

have taken change in the sintering process. At the early stage of sintering, the neck and the stomata among the particles are filled with material; the volume of the pore decreases and the neck grows up gradually. The grain boundaries begin to form gradually among the fine particles, the area is enlarged constantly, and the gel tends to be densified. At the late stage, with the increase

of calcining temperature, the bonding of particles becomes more evident, and the grain grows, too.

3.3 Effect of calcining temperature on luminescent characteristics of phosphor powder

The excitation and emission spectra of YAG phosphor prepared by sol-gel low-temperature

combustion method at different calcining temperatures are shown in Fig.6.

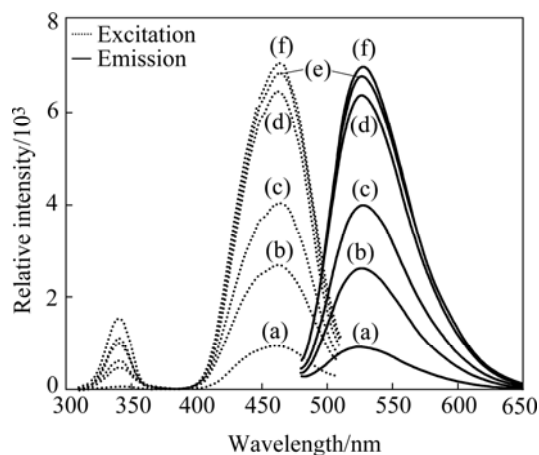


Fig.6 Excitation and emission spectra of sample at different temperatures: (a) 800 °C; (b) 900 °C; (c) 1 000 °C; (d) 1 100 °C; (e) 1 200 °C; (f) 1 300 °C

From Fig.6, a double peak structure that locates at ultraviolet (340 nm) and visible blue light (460 nm) is its excitation spectrum, and its emission peak is at around 530 nm, corresponding to the light produced by the transition of 5d to 4f states of Ce^{3+} . The peak location remains basically unchanged as the calcining temperature increases gradually. This is because the crystal particle size does not affect the emission photon energy by the transition of its 5d to 4f states, thus the emission peak remains at around 530 nm. But peak value and peak area of both the excitation and emission spectra of the phosphor increase gradually with the increase of calcining temperature, which agrees well with the experiment result of the XRD analyses above, namely, with the increase of calcining temperature, the particles transform from amorphous to crystalline, and become more and more consummate. As shown in Fig.5, the higher the calcining temperature is, the larger the particle size of YAG:Ce^{3+} phosphor is, and the greater the luminous intensity is. All of these indicate that the particle size of the sample has a great effect on the luminous intensity. This is mainly because the crystalline area and the light-emitting region increase with the increase of the particle size. On the contrary, the smaller the particle size is, the larger the specific surface area is, and the more defects the surface has. Therefore, the absorption of excited light and the luminescence will be decreased. When the temperature is 1 300 °C, the particle size approaches micron scale. And if the temperature increases further to exceed the solid-state reactions point, the luminescent properties will be decreased because of the severe agglomeration of the particles and the uneven distribution of grain size. Then it will need a secondary

crushing, which increases the producing cost.

4 Conclusions

1) The precursors are prepared by sol-gel low temperature combustion method using nitrate and yttrium oxide as raw materials, citric acid as complexing agent, at pH=2 and $n(\text{M})/n(\text{C})=2.0$, then they are calcined at 1 300 °C, and YAG:Ce^{3+} phosphors with high crystallinity, ultra-fine in size and uniform morphology can be obtained.

2) The YAG:Ce^{3+} phosphor is obtained by sintering the precursors at 800 °C, and pure phase of YAG is formed without YAM, YAP or other mesophase existed. Also, the crystallinity increases and the particle grows up gradually with the increase of the calcining temperature.

3) A double peak structure that locates at ultraviolet (340 nm) and visible blue light (at around 460 nm) is the excitation spectra of the phosphor. And its emission spectrum is at around 530 nm. With the gradual increase of the calcining temperature, the peak location of excitation and emission spectra remain unchanged, but its relative intensity increases gradually.

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