O U R N A L O F

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# Study of co-excited green emission of Tb<sup>3+</sup>, Ce<sup>3+</sup> and Gd<sup>3+</sup> in yttrium aluminum garnet

Fei Huang<sup>a</sup>, Limin Dong<sup>b</sup>, Zhengyi Fu<sup>a,\*</sup>, Hao Wang<sup>a</sup>, Weimin Wang<sup>a</sup> and Yucheng Wang<sup>a</sup>

<sup>a</sup>State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, P.R.China

<sup>b</sup>School of Material Science & Engineering, Harbin University of Science and Technology, Harbin 150040, P.R.China

YAG :  $Tb^{3+}$ ,  $Ce^{3+}$ ,  $Gd^{3+}$  nano-phosphors derived from a sol-gel chemistry have been successfully synthesized and characterized by TG/DTA, XRD, SEM, and spectrometer. The results show that the phosphors have a uniform particle size distribution ranging 30-50 nm. The value of the lattice constant increased with an increase of the  $Gd^{3+}$  content.  $Tb^{3+} \rightarrow Ce^{3+}$ ,  $Ce^{3+} \rightarrow Tb^{3+}$ and  $Gd^{3+} \rightarrow Ce^{3+}$  energy transfer existed in the co-excited system. The luminescence intensity was controlled by the concentration and ratio of the co-dopants. A small quantity of  $Gd^{3+}$  and  $Ce^{3+}$  evidently increased the green emission ( ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ ) of  $Tb^{3+}$ .

Keywords: Sol-gel, YAG, nano-phosphor, energy transfer.

### Introduction

Owing to their stable lattice structure and large thermal conductivity, yttrium aluminum garnet (Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>, YAG) materials have been widely studied for their potential application in the fields of luminescence and solid state lasers [1-4]. YAG is a superhard material and can't be damaged easily under a highly irradiant electron beam. Therefore, rare-earth-doped YAG materials, such as Tb, Eu, Cr, Ce and Tm, are promising phosphor candidates in cathode-ray tubes (CRTs), field emission displays (FED), plasma display panels (PDP), etc. In particular, YAG : Tb<sup>3+</sup> has been studied extensively due to its well known green emission. Recently, co-doped rare earth phosphors have been studied because the energy transfer and migration can enhance the luminescent intensity [5-6]. Shmulovich, Liu and their co-workers have studied co-excitation of Ce<sup>3+</sup> and Tb<sup>3+</sup> in YAG host materials. However, to the best of our knowledge, there is little literature about coexcited phosphors of  $Ce^{3+}$ ,  $Tb^{3+}$  and  $Gd^{3+}$  in YAG [7-8].

Conventionally, YAG materials are prepared by solid state reactions using yttria ( $Y_2O_3$ ) and alumina ( $Al_2O_3$ ) as starting materials. The process involves extensive heat treatments at high temperatures (> 1800 °C) and repeated mechanical mixing to achieve the pure garnet structure. So the particle size becomes very large at such high temperatures and long holding time. Before using, it needs to be ground, however, the treatment process will

easily destroy the structure and deteriorate the performance of the luminescence [9-11]. Recently, some new wet chemical methods have been developed to achieve YAG material with a fine grain size, such as hydrothermal synthesis, a sol-gel process, spray pyrolysis, co-precipitation, *etc.* Among these methods, the sol-gel route is one of the most important process because of its advantages: lowtemperature synthesis, composition homogeneity, good crystallization, uniform grain size, material design with versatile compositions and good morphology [12-15].

Based on the above consideration, YAG :  $Tb^{3+}$ ,  $Ce^{3+}$ ,  $Gd^{3+}$  phosphors were synthesized by a sol-gel process in this studies.  $Ce^{3+}$  and  $Gd^{3+}$  were used as sensitizers for the  $Tb^{3+}({}^{5}D_{3})$  luminescence. The factors influencing luminescence were also discussed in detail.

### **Experiment Process**

#### **Experiment method**

 $Y_3Al_5O_{12}: Tb^{3+}$ ,  $Ce^{3+}$ ,  $Gd^{3+}$  nano-phosphors were synthesized by sol-gel chemistry using Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Ga(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and citric acid as starting materials. All the starting materials were analytic grade and purchased from Shanghai Chemical Reagent Incorporation. Firstly, the above reagents were weighted according to the stoichiometrics of Y<sub>2.8</sub>(Ce<sub>0.12</sub>Tb<sub>0.08</sub>)Al<sub>5-x</sub>Gd<sub>x</sub>O<sub>12</sub> (x = 0.1-1.0). Citric acid was used as a chealating ligand and all the nitrates were dissolved in deionized water, and then the nitrate solutions were added to the citric acid solution slowly with energetic stirring. The molar ratio between total metallic ion and citric acid was kept at 1 : 1.2. An ammonia solution was used to adjust the pH value of

<sup>\*</sup>Corresponding author:

Tel : +86-027-87865484

Fax: +86-027-87215421

E-mail: zyfu@whut.edu.cn

the solution to 8. After overnight with constant stirring at 75 °C, a clear homogeneous YAG :  $Tb^{3+}$ ,  $Ce^{3+}$ ,  $Gd^{3+}$  solution was obtained. This clear solution was made into a gel by baking to evaporate the solvent at 60 °C for two days and then dried at 110 °C for about 8 h. Subsequently, the precursors were annealed at various temperatures with a heating rate of 10 Kminute<sup>-1</sup>.

## Characterization techniques

The phases in the final products were established using a D/MAX-rB X-ray diffractometer (Rigaku Incorporation, Japan) with Cu K $\alpha$  radiation ( $\lambda$  = 1.54178 Å). The scanning rate was 4°minute<sup>-1</sup>. The morphology was characterized by a Sirion 200 scanning electron microscope (FEI Incorporation, Holland) and JSM 5610Lv scanning electron microscope (JEOL Incorporation, Japan). Thermal analyses were undertaken on a STA 449C thermal analyzer (METZSCH Incorporation, Germany) and the samples were heated from room temperature to 1400 °C at 10 Kminute<sup>-1</sup>. The luminescence spectra were recorded with a FP-6500 spectrometer (Jasco Incorporation, Japan).

### **Results and Discussions**

## Phase analysis of the sample

A TG curve and a DTA curve of the precursor gel are shown in Fig. 1. It can be seen that the total mass loss is about 85% from the TG curve. There are three key stages of mass loss, the first stage (about 70%) is the volatilization of adsorbed water and combined water below 300 °C, and this stage is very rapid. The second stage (about 12%) is the decomposition of citric acid salt in the range of 400 °C-600 °C. The third stage (about 3%) is the formation of the YAG phase in the range of 800 °C-1000 °C. There is no significant mass loss above 1000 °C. In the DTA curve, there are three exothermic peaks: 261.8 °C, 447.6 °C and 823.8 °C. They correspond to the removal of combined water, decomposition of citric acid salt and formation of YAG, respectively. Furthermore,



Fig. 1. The thermal analysis profiles of the precursor gel.



Fig. 2. XRD patterns of the samples heat-treated at different temperatures.

the exothermic peak at about 823.8 °C is the onset of YAG crystallization.

Fig. 2 shows the XRD patterns of the samples heattreated at different temperatures. The peaks of YAG are not found at 700 °C, which indicates that the sample is amorphous and agrees with the thermal analysis. At 900 °C, the YAG peaks are found. This indicates the formation of the YAG phase. However, YAlO<sub>3</sub> (YIG) and Al<sub>2</sub>O<sub>3</sub> interphases are also found in the XRD pattern. At 1050 °C, the fully-crystallized phase is identified as the pure YAG structure. Traditionally, the synthesis temperature of solid-state sintering methods is higher than 1800 °C. Apparent structural changes can be found after Gd was doped because of the larger d value, and a small shift can be observed toward lower  $2\theta$  values with respect to the standard pattern. This can be explained in terms of an expansion in the crystallographic unit cell owing to the gadolinium dopant with a larger radius.

# Morphology characterization

Typical scanning electron microscope (SEM) images of  $Y_{2.8}(Ce_{0.12}Tb_{0.08})Al_{5-x}Gd_xO_{12}$  (x = 0.6) precursor and its final nano-phosphor are shown in Fig. 3. The precursor is the net structure of citric acid, and the powders are very large. The final product at 1050 °C is about 30-50 nm, which is far smaller than the products prepared by solid state reactions. It can be observed that the phosphors exhibit in general uniform grain size. This is required for good brightness during their processing. Meanwhile, the morphology is similar and nearly spherical. It is known that the use of spherical phosphors should increase the screen brightness and improve the resolution because of lower scattering and higher packing densities.

## Luminescence properties

Fig. 4 shows the PL spectrum of Y<sub>2.8</sub>(Ce<sub>0.12</sub>Tb<sub>0.08</sub>)Al<sub>5-x</sub>



**Fig. 3.** SEM images of the samples. (a) precursor of the powders; (b) the final products treated at 1050 °C.



**Fig. 4.** PL spectrum of YAG :  $Tb^{3+}$ ,  $Ce^{3+}$ ,  $Gd^{3+}$  phosphor.

 $Gd_xO_{12}$  (x = 0.6) phosphor at 1050 °C. From the spectrum, it is seen that the adsorption spectrum is at about 270 nm. The emission spectra at 486 nm, 542 nm, 584 nm and 626 nm correspond to the energy transition of  ${}^5D_4 \rightarrow {}^7F_6$ ,  ${}^5D_4 \rightarrow {}^7F_5$ ,  ${}^5D_4 \rightarrow {}^5F_4$  and  ${}^5D_4 \rightarrow {}^7F_3$  respectively. Of these,



Fig. 5. The intensity change of luminescence with the content of gadolinium.

the energy transition of  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  is the strongest at 542 nm, which is a typical green emission. However, it is split into two peaks because of the influence of the crystal field. The energy transition of  ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$  at 486 nm is secondary, which has deleterious effect on the green phosphor. Therefore, a strong emission of  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  and a weak emission of  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  are needed for green phosphors.

Fig. 5 shows the effect of Gd content on the luminescent property. The intensity of  ${}^5D_4 \rightarrow {}^7F_5$  increases with an increase of the Gd content initially and reaches a maximum at x = 0.6, then decreases. However, the intensity of  ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$  decreases with an increase of the Gd content initially, and then increases. Because the  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  emission directly decides the property of the YAG : Tb<sup>3+</sup>, Ce<sup>3+</sup>, Gd<sup>3+</sup> green phosphor, a strongest emission at  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  and a weakest emission at  ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$  are needed. Based on the above viewpoint, the performance of YAG :  $Tb^{3+}$ ,  $Ce^{3+}$ ,  $Gd^{3+}$  green phosphor is the best when x is 0.6. The reason may be caused by the competition between Ce ions and Gd ions. When the content of Gd ions is very low, Gd can assist Ce ions to absorb excitated energy, then transfer it to Tb ions to emit green luminescence. However, the Gd ions and Ce ions compete in absorbing excited energy when the content of Gd continues to increase, and Gd ions blocks the absorption by Ce ions. So the emission of  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  decreases and the emission of  ${}^{5}\text{D}_{4} \rightarrow {}^{7}\text{F}_{6}$  increases.

#### Conclusions

YAG: Tb<sup>3+</sup>, Ce<sup>3+</sup>, Gd<sup>3+</sup> nano-phosphors were prepared by a sol-gel method at 1050 °C, which is lower than the temperature for traditional method. The particle size was about 30-50 nm and the morphology was nearly spherical. The excited spectrum is at about 270 nm and the main emission spectrum is at 542 nm. The luminescent intensity of green emission increases with Gd content initially, then decreases. When the content of Gd is 0.6, the green luminescence is optimal owing to the co-excited effect of Ce ions and Gd ions. The reason for this is a competition between Ce ions and Gd ions.

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