Research of Luminescent Properties on Eu^{3+} Doped YAG

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***Abstract*—Using rare earth oxides, aluminum nitrate and gelatin as raw materials, YAG:Eu^{3+} based luminescent materials were successfully synthesized by gel-network co-precipitation method. The formation and luminescent properties of YAG: Eu^{3+} was investigated by means of fluoresce spectra. For YAG:Eu^{3+}, the differences for the excitation and emission spectra of Eu^{3+} in the amorphous and crystalline states of YAG were observed, and the emission intensities increased with the increase of calcinated temperature. The effect of Bi^{3+} on the sensitization of Eu^{3+} in YAG host was also observed.**

Keywords-Luminescent properties; Eu^{3+} doped YAG; Fluoresce spectra

I. INTRODUCTION

YAG garnet phases have been widely used as a host material for lasers and phosphors for their excellent luminescent properties and stable physical and chemical properties [1-2]. Recently, YAG doped with a small amount of element such as Eu, Ce and Tb has been evolved due to a widely utilized photonic application of such phosphors in the area of CRTs and LED [3-7].

II. EXPERIMENTAL

A novel low temperature synthesis technique for nanocrystalline garnet phosphors using a gelnetwork- co-precipitation method is reported [8]. The samples prepared in this work were designed to have an overall composition $Y_{3-0.2-x}Al_5O_{12}:Eu_{0.2}$, Bi_x (x = 0 or 0.002). Y_2O_3 and Eu_2O_3 (99.99% pure, Shanghai Yuelong New Materials Co. Ltd.), $Al(NO_3)_3\cdot 9H_2O$,$NH_3\cdot H_2O$ and $Bi(NO_3)_3\cdot 5H_2O$ (analytical grade, Beijing Shuanghuan Weiye Reagent Co. Ltd.), and gelatin (chemical purity Cangzhou Jinjian gelatin Co. Ltd.) were used as starting materials. Aqueous nitrate solutions of rare earth ions were prepared by dissolving high-purity Y_2O_3 and Eu_2O_3 in HNO_3 then diluting with deionized water. 25mL of 0.2 $mol\cdot L^{-1}$ aluminum nitrate solution was mixed uniformly with 14mL of 0.2 $mol\cdot L^{-1}$ yttrium nitrate and 2mL of 0.1$mol\cdot L^{-1}$europium nitrate solution in a beaker under stirring. Then 6g gelatin was dissolved in the above mixed nitrate solution with vigorous stirring at 80°C heating in water bath for 2h.Then the mixture turn to a yellowish gel when it was cooled to 4°C. Cutting the gel into small pieces and soaked in saturated 6 $mol\cdot L^{-1}$ $NH_3\cdot H_2O$ solution for 24 h at 4°C. Then the hydroxides were co-precipitated in the gelnetwork. Washed gel with cooled distilled water to remove nitrate ions and residual ammonia, and dried in a vacuum chamber at 110°C. The dried gel (called the "precursor'') was preheated at 400°C for 2 h in the air. After an intermediate grinding, the powder was subsequently fired at various temperatures from 500 to 900°C for 3 h in a muffle furnace in the air, producing fine phosphor powders.

The photoluminescence spectra of phosphors were measured on a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

III. RESULTS AND DISCUSSION

A.The characterization of luminescent properties

The photoluminescence spectrum of the samples calcinated at 600°C and 900°C were measured at room temperature, as shown in Fig.1and Fig.2, respectively. In the excitation spectrum, the strongest sharp peak appeared at 395 nm, corresponding to the characteristic absorbed lines of the electron transition of Eu^{3+}ions ($^7F_0\rightarrow{}^5L_6$). While the other weak excitated peaks are obtained at 323 nm ($^7F_0\rightarrow{}^5H_6$)、365 nm ($^7F_0\rightarrow{}^5D_0$)、385 nm ($^7F_0\rightarrow{}^5G_2$) and 418 nm ($^7F_0\rightarrow{}^5D_3$). In addition, the excitation band in the range of 220-270 nm is consistent with the charge transition of Eu^{3+} from the ground state $^7F_0$ to the transfer state. It can be seen that the main emission peaks appeared at 582, 592, 597, 611 and 633 nm, which is corresponding to the transition of $^5D_0\rightarrow{}^7F_0$, $^5D_0\rightarrow{}^7F_1$, $^5D_0\rightarrow{}^7F_2$ and $^5D_0\rightarrow{}^7F_3$ of the Eu^{3+} using 395 nm ultraviolet as the excitation wavelength at room temperature. It is worth noted that the transition spectral line of $^5D_0\rightarrow{}^7F_1$ and $^5D_0\rightarrow{}^7F_2$ are the sensitive lines of the Eu^{3+} in the crystal. The chemical environment of the Eu^{3+} could be analyzed qualitatively according to the relative intensity ratios of the two sensitive lines.

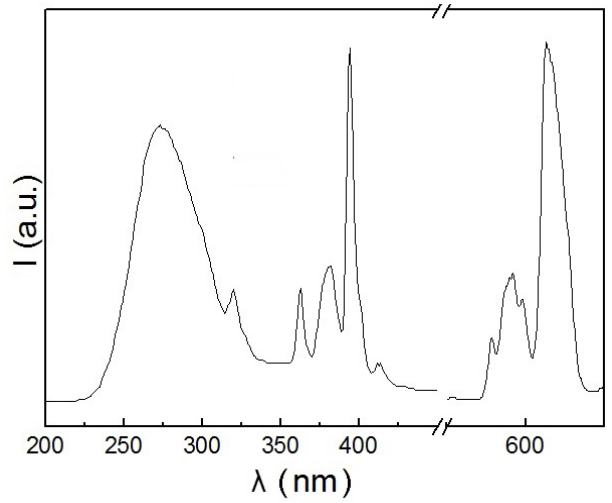

Figure 1. Excitation and emission spectral of sample calcations at 600°C (λem=612nm, λex=395nm)

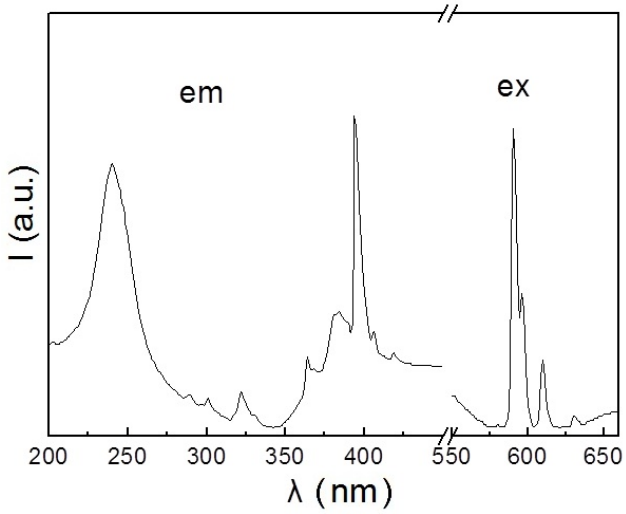

Figure 2. Excitation and emission spectral of sample calcations at 900°C (λem=592nm, λex=395nm)

B. Effect of calcination temperature on the luminescent properties

The effect of the calcination temperature on the luminescent properties of the YAG:Eu^{3+} can be divided into two stages: the one is from the amorphous to the phase before the crystallization, and the other is the phase after the crystallization. The spectral characteristics of the YAG: Eu^{3+} have changed dramatically from the amorphous to the crystallization. But after the crystallization, the spectral characteristics have changed little except for the relative intensity. Fig.1and Fig.2 show the excitation and emission spectra of samples calcinated at 600°C and 900°C, respectively.

The excitation spectra of these two samples are composed of the sharp peaks of f→f electronic forbidden transition, which are ascribed to Eu^{3+}-O^{2-} transfer state and the $4f^6$ electronic configuration of the Eu^{3+} at the range of far-ultraviolet region. The strongest sharp peak appearing at 395 nm belongs to $^7F_0 \rightarrow {}^5L_6$ electron transition of the Eu^{3+} ions.

The highest peak of the charge transfer of $Eu^{3+}$is located at 273 nm for the sample calcinated at 600°C, while it is appeared at 240 nm for the sample calcinated at 900°C. In addition, the f→f excitation line-spectrum of the sample calcinated at 900°C is sharper than that of the sample calcinated at 600°C. Generally, the energy position of charge transmission site (CTS) of the Eu^{3+} is related to the Eu^{3+}-O^{2-} bond covalent and the symmetry number of the Eu^{3+}. The higher the Eu^{3+}-O^{2-} bond covalent is, the lower the energy position will be.

The bond covalent of Eu^{3+}-O^{2-} is affected by another metal ion M^{3+} (M^{3+}=Y^{3+}, Al^{3+}) adjacent to O^{2-} in YAG. In the amorphous and crystallization of YAG, the possibilities of the interactions between the bond of Eu^{3+}-O^{2-} and M^{3+} are Eu^{3+}-$O^{2-}_{(1)}$…M^{3+} and Eu^{3+}-$O^{2-}_{(2)}$-M^{3+}, respectively ("…" presents the chemical bonds which have not been formed, or initial formed, "-" presents the strongly chemical bonds formed). So the electron cloud density of $O^{2-}_{(1)}$ are higher than that of $O^{2-}_{(2)}$, which lead to result that the electron transfer are easier from the O^{2-} in the bond of Eu^{3+}-$O^{2-}_{(1)}$to the Eu^{3+} than that in the bond of Eu^{3+}-$O^{2-}_{(2)}$. Namely, the CTS of the Eu^{3+} ion has lower energy position in the amorphous state compared with the crystallized state. Moreover, the Y^{3+} (Eu^{3+}) has higher degrees of symmetry in the amorphous state than that in the crystallized state, which should be beneficial for CTS of Eu^{3+} to transfer to lower energy position.

The $^5D_0 \rightarrow {}^7F_J$ emission spectrum of the sample can be gotten by using 395 nm as light source. It can also found that the emission line of the sample calcinated at 900°C is sharper than that at 600°C. For the sample calcinated at 600°C, red emission peaks could be obtained at 613 nm and 579 nm. The emission peak at 613 nm was caused by the electric dipole transition ($^5D_0 \rightarrow {}^7F_2$), while the emission peak at 579 nm might be formed by the transition ($^5D_0 \rightarrow {}^7F_0$). This result illustrated that most of the Eu^{3+} ions were in the inversion symmetry C_s, C_n, C_{nv} cells. For the sample calcinated at 900°C, it appeared orange light at 592 nm, which means that the electric dipole transition ($^5D_0 \rightarrow {}^7F_1$) was in a dominant position and the transition ($^5D_0 \rightarrow {}^7F_0$) disappeared. There is no significant difference in the excitation and emission spectrum for the samples calcinated between 700 and 900°C except for the relative intensity.

The $^5D_0 \rightarrow {}^7F_2$ transition of the Eu^{3+} is belong to ultrasensitive transition, and easily affected by external environment. The environment of Eu^{3+} in the amorphous state is obviously different from the crystalline state, so the sites are also changed. This will lead to that the emission lines of the Eu^{3+} in the crystalline state are widened a lot than that in the amorphous state. Meanwhile, the distribution of the Eu^{3+} ions in the amorphous samples are

irregular and the symmetry of the Eu^{3+} is low. Above all, the dipole transition ($^5D_0 \rightarrow {}^7F_2$) at the forbidden point has high intensity. However, the Eu^{3+} could occupy the sites of the Y^{3+}, which lead to a significant reduction of transition strength ($^5D_0 \rightarrow {}^7F_2$). Namely, the emission ratio of red versus orange will be significantly reduced from the amorphous state to the crystalline state. The reason why the spectra have significant differences between the samples treated at low and high temperatures is given below. When the sample was treated at 600°C, the crystallinity was low and the content of impurities was high, which result in an entirely different chemical environment compared with the sample treated at 900°C. When the calcined temperature was over 700°C, the samples were complete crystallization. So the excitation and emission spectra of Eu^{3+} have changed little except for the relative intensity.

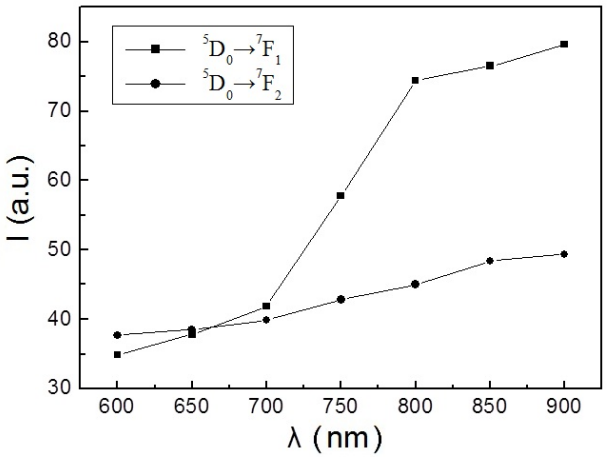

Figure 3. Emission intensity as a function of calcinations temperature

Fig.3 shows the curves of luminous intensity to wavelength for samples treated at different temperatures. It can be seen that the transition emission intensity of $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ increase as the temperature is raised. This is because that with the temperature increasing, the content of the impurity is reducing, and the crystallization of the sample is increasing.

C. Effect of Eu^{3+} concentration on luminescent properties

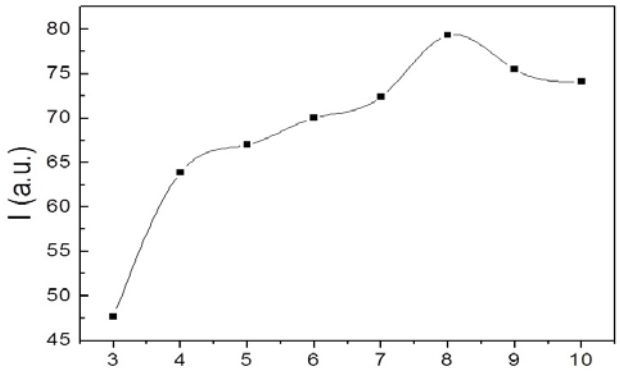

Figure 4. Emission intensity as a function of Eu^{3+} concentration

Fig.4 shows the relationship between the luminous intensity at 592 nm and Eu^{3+} concentration using 395 nm ultraviolet as the excitation sources. With the Eu^{3+} concentration increasing to 8%, the luminous intensity gradually increases and reaches a maximum. With the Eu^{3+} concentration further increasing, the luminous intensity decreases and even quenches.

D. Effect of Bi^{3+} concentration on luminescent properties

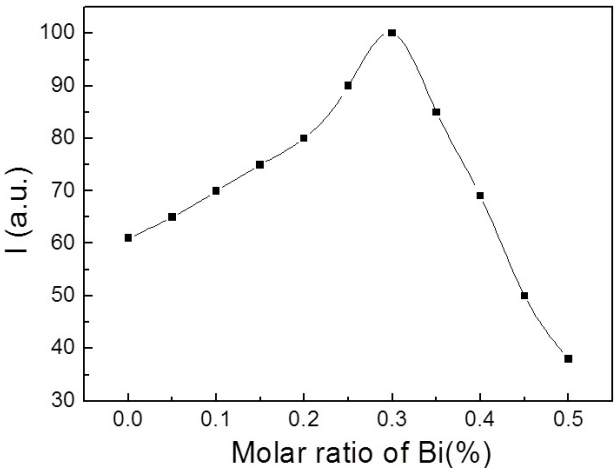

Figure 5. Emission intensity as a function of Eu3+ concentration

In order to increase the performance and reduce the cost of the Eu^{3+} doping phosphor, we studied the effect of Bi^{3+} on the sensitized luminescence of the Eu^{3+} in the YAG substrate, as shown in Fig.5. It was suggested that the luminous intensity is the strongest in the double doping system when the doping concentration of the Bi^{3+} is 0.3% in the sample of 6% YAG:Eu^{3+}.

The broadband emission peak of Bi^{3+} appeared in the wavelength from 300 nm to 500 nm. The strongest peak appeared at 393nm, which was corresponding to the electron transition of $^3P_1$-$^1S_0$. It was overlapped with the stimulated peak of the Eu^{3+}, and the necessary condition of reabsorption of light and resonance energy transfer was reached. The reabsorption of light was excited by the emission light from sensitizing agent absorbed by activating agent. So, with the increasing of the adding amount of Bi^{3+}, the luminous intensity is sharply enhanced. However, excessive amount of Bi^{3+} will also lead to the quenching of luminous intensity.

IV. CONCLUSIONS

In conclusion, the gel-network co-precipitation method is so successfully in synthesizing YAG:Eu^{3+} for its low synthesis temperature and simple instruments. As for YAG:Eu^{3+}, the differences for the excitation and emission spectra of Eu3+ in the amorphous and crystalline states of YAG were observed, and the emission intensities increased with the increase of calcinated temperature. The highest peak of the charge transfer of $Eu^{3+}$is located at 273 nm for the sample calcinated at 600°C, while it is appeared at 240

nm for the sample calcinated at 900°C. In addition, the f→f excitation line-spectrum of the sample calcinated at 900°C is sharper than that of the sample calcinated at 600°C. The effect of Bi^{3+} on the sensitization of Eu^{3+} in YAG host was also observed.

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