Preparation and photoluminescence study of Alumin o-boro silicate YAG fluorescent glass for White LED

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Abstract

The YAG: Eu³⁺ fluorescent glass for NUV(near ultraviolet) white LEDs was obtained firstly by synthesizing Y₃Al₅O₁₂ (YAG): Eu³⁺ precursors through a simple co-precipitation method, and then mixing precursor with B₂O₃-Al₂O₃-SiO₂-Na₂O-BaO glass powder calcined at 1400°C for 2.5 hours. The as-prepared YAG glass-ceramic phosphor was investigated by DTA, XRD, SEM, and photoluminescence (PL). Influence of YAG: Eu³⁺ precursor and Eu³⁺ doping on excitation and emission spectra also have been studied. The results show that: the phosphor's emission peak located at 393nm is correspond to the ⁷F₀ - ⁵L₆ transition of Eu³⁺ ions, which matches good with UV LED chips; the phosphor gives intense emission at 593nm originating from the ⁵D₀ - ⁷F₁ transition of Eu³⁺ ions. When the YAG precursor is 0.9g and amount of Eu³⁺ doped is 0.08, the fluorescence excitation spectra of glass and emission spectra of the peak intensity reach its maximum value. The YAG: Eu³⁺ fluorescence glass could be a promising material for the production of near ultraviolet chip white light-emitting diode.

Introduction

White light emitting diode light source with a low driving voltage, applicability, high stability, short response time, mercury and lead pollution, monochromatic light etc., will be the most promising lightning source, which will replace the incandescent, fluorescent, high intensity gas discharge lamp in the 21 century [1,2]. Currently people use blue LED chip coated with yellowish phosphor of YAG to achieve white LED, its color temperature is usually higher than 5000K, the general color rendering index also is less than 80. Optical parameter of white LEDs will change after a period time of using as the light-emitting chip and phosphors have different life span; additionally, when the phosphor is heated by LED chips, it will accelerate phosphor deterioration, luminousness of organic encapsulating material also will decline, making the life span of white LED decrease [3,4,5]. Although RGB LED chips of white LED have relatively wide and low color temperature range, it can easily achieve high color rendering index, but the RGB chips have different light attenuation coefficient, it needs to add appropriate control circuit [1,6,7].

Using near-UV chips as excitation source to excite tribasic fluorescent powder has become a n international hot spot recently [8,9,10]. As the visual sensitivity of the near-UV is not obvious to human, we can achieve high color rendering index in a large range of color temperature. Near-UV excitation white LED is considered to lead new generation of white LED lighting direction [11,12]. YAG is widely used as laser and light-emitting substrate material for its excellent physical and chemical properties[13]; YAG phosphors doped with Eu³⁺ ions have a strong excitation peak in 395nm, which matches good with exciting wave band of near-UV LED chips and emit bright orange-red shade. The phosphor fluorescent glass makes excellent heat distribution in the glass material, which approximately equal to phosphor remote technology. Fluorescent glass has following advantages: simple production process, high light efficiency, low luminescence decay [14,15,16,17]. In this work we have prepared YAG: Eu³⁺ fluorescence glass in B₂O₃-Al₂O₃-SiO₂-Na₂O-BaO system, its spectral properties, light-emitting properties also have been studied.

Materials And Methods

2.1 materials

Eu_2O_3 (99.99%), Y_2O_3 (99.99%), $\text{NH}_3\cdot\text{H}_2\text{O}$ (25-28%), HNO_3 (65-68%), $\text{CH}_3\text{CH}_2\text{OH}$ (99.7%), $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (AR), NH_4HCO_3 (AR), Al_2O_3 (AR), Na_2CO_3 (AR), SiO_2 (AR), H_3BO_3 (AR), BaCO_3 (AR) were used as starting materials.

First yttrium oxide and europium oxide were dissolved in dilute nitric acid respectively to obtain yttrium nitrate, europium nitrate and aluminum nitrate with concentration of 1mol/L metal ions solution. Then mix the above three kinds of solutions according to yttrium aluminum garnet $\text{Y}_{3-x}\text{Eu}_x\text{Al}_5\text{O}_{12}$ ($x = 0, 0.02, 0.04, 0.06, 0.08, 0.1$) stoichiometric. Prepare 100mL mixed precipitant with the composition of $\text{NH}_3\cdot\text{H}_2\text{O}$ 2mol/L and NH_4HCO_3 2mol/L, then mix the three metal ion source by fap funnel with 3mL/min into mixed precipitator with constant temperature at 30°C. Adjust mixture pH to 6.5 with ammonia swap around, then continue stirring 2h, aging for 12h; Discard the supernatant after centrifugation, wash precipitate precursor with deionized water four times, with ethanol three times, then put precipitate precursor into constant temperature oven with 120°C for 12h, obtain YAG: Eu^{3+} precursors by grinding at last[16].

The initial composition of the glass materials are BaCO_3 0.54g, Na_2CO_3 0.217g, H_3BO_3 0.478g, SiO_2 0.164g, Al_2O_3 0.3g, add YAG precursor (0.7g, 0.8g, 0.9g, 1.0g, 1.1 g), and anhydrous ethanol. Grind these raw materials together for a long time, put the material into corundum crucible after drying, then put corundum crucible into atmosphere resistance furnace for 7h, insulate 2.5h when the temperature reached 1400°C, casting forming the sample in a muffle furnace after 550°C annealing 3h. Polish sample to form 1cm*1cm thin transparent fluorescent glass [16,17].

2.2 Characterization of YAG: Eu^{3+} Glass-ceramic

Sample's crystal structure was scanned by ARL TRA X-ray diffraction (XRD). YAG precursor, the glass base and their mixture were analyzed with differential thermal analysis (DTA) by Netzsch STA-449F3 thermal analyzer. Sample morphology was scanned with Hitachi S3400 scanning electron microscope (SEM). Sample's excitation and emission spectra were measured by RF-5301PC fluorescence spectrophotometer.

Results And Discussion

3.1 DTA-TGA analyze of YAG: Eu^{3+} fluorescent glass

Fig.1 shows the DTA-TGA curves of precursor during the calcination process. The precursor sample was synthesized by 1.74g H_3BO_3 - SiO_2 - Al_2O_3 - Na_2CO_3 - BaCO_3 adding 0.9g $\text{Y}_{2.94}\text{Eu}_{0.06}\text{Al}_5\text{O}_{12}$ by co-precipitation method. We can see that YAG precursor materials and glass initial homogeneous mixture loss 38% weight from room temperature to 300°C, there is an endothermic peak at 68.4°C corresponding to the initial precursor materials and glass adsorption water loss; and there is a sharp endothermic peak at

203.8°C, corresponding to the apparent weight loss TGA curve, which is the initial glass material loss of the crystal water. From 300°C to 1400°C, there are about 40% weight loss and endothermic peak appeared separately at 662.7°C, 818.2°C and 938.7°C, etc. There is more than one endothermic peak, which ascribe to the decomposition of boric acid and carbonate compounds, subsequent exothermic peak and formation of YAG crystal phase.

3.2 XRD analyze of YAG: Eu³⁺ fluorescent glass

The Y_{2.94}Eu_{0.06}Al₅O₁₂ fluorescent glass was synthesized by 1.74g glass material and 0.9g precursor, its XRD patterns was correspond with Y₃Al₅O₁₂ standard map (PDF:79-1892). We can certificate that the crystal in glass-ceramic was YAG, which belong to body-centered cubic crystal system. The diffraction have relatively sharp peaks, which indicate that a small amount of rare earth ions Eu³⁺ replaces Y of the crystal lattice and crystallization of YAG phase was well mixed, and it does not affect the formation of YAG phase [15,16,18]; Fig.2 shows the XRD patterns of glass material without YAG: Eu³⁺ glass precursor. There are not obvious diffraction peaks in the photo, which certificated that products have amorphous form.

3.3 Excitation and emission spectra of YAG fluorescent glass

3.3.1 Influence of YAG fluorescent glass spectral characteristics under different content of YAG precursor

Fig.3 and Fig.4 show the excitation and emission spectra of fluorescent glass with different quality (0.7g, 0.8g, 0.9g, 1.0g and 1.1g) of Y_{2.94}Eu_{0.06}Al₅O₁₂ precursor. The excitation spectra of YAG: Eu³⁺ fluorescence glass was detected at wavelength of 593nm, test range was 350 ~ 420nm. The strongest excitation peak was at 393nm, correspond to ⁷F₀-⁵L₆ transition of Eu³⁺ ions, which belong to Eu³⁺ Characteristic absorption lines. The excitation spectra matches good with exciting wave band of near-UV LED chips, the other weak excitation peaks were ⁷D₀-⁵G₂ transition (peak at 381nm) and ⁷F₀-⁵D₃ transition (peak at 416nm), etc. [17].

Fig.3 Excitation spectra of fluorescent glass with different content of precursor

Emission spectra was detected at wavelength of 393nm, test the range was 575 ~ 635nm. The strongest peak appears at 593nm (⁵D₀-⁷F₁), which belong to the same transition with ⁵D₀-⁷F₁ transition at 598nm, emission spectra was orange. There are also two weak emission peak at 611nm and 631nm, correspond to the ⁵D₀-⁷F₂ transition and the ⁵D₀-⁷F₄ transition. Symmetrical Y³⁺ ions were replaced by Eu³⁺ ions In YAG crystal, so the emission peak is based on the magnetic dipole ⁵D₀-⁷F₁ transition (at 593nm) [17].

The peak wavelength of excitation and emission spectra of YAG fluorescent glass with different content of YAG precursor almost not change, but the spectra intensity have changed.

When the content of YAG precursor is between 0.7 ~ 0.9g, the intensity of excitation and emission peaks increased; while the content of YAG precursor is between 0.9 ~ 1.1g, the intensity of excitation and emission peaks decreased. When the content of YAG precursor is 0.9g, the intensity of excitation and emission peaks reaches their maximum value. The change of precursor content lead to the excitation and emission peaks rise and fall as the initial mixture of materials and YAG glass precursor composition contains Al_2O_3 . When the YAG precursor content decreased, during the high-temperature calcination process, Al_2O_3 in precursor will partly enter the glass base and become glass components, resulting in YAG crystal phase formation reducing. When the content of YAG: Ce^{3+} precursor is more than 0.9g, it led glass formation process decline. When the content of YAG: Ce^{3+} precursor is 1.0 and 1.1g, the vitreous loss through impact excitation and emission light reaches phosphor escape fluorescent glass surface, resulting in excitation and emission spectra intensity decreased [16].

3.3.2 Eu^{3+} doped YAG fluorescence of the spectral characteristics of glass

While keeping the calcination temperature at 1400°C for 2.5h and other experimental conditions unchanged, we changed the x value of the $\text{Y}_{3-x}\text{Eu}_x\text{Al}_5\text{O}_{12}$ ($x = 0.00 \sim 0.1$) fluorescent glass, then test the excitation and emission spectral of fluorescent glass. Fig.5 and Fig.6 show the excitation and emission spectra of YAG fluorescent glass with the x value under 0.00, 0.02, 0.04, 0.06, 0.08, 0.1.

It can be seen from the Fig.5 and Fig.6 that the excitation and emission spectra of the sample is composed by a set of spikes. As the x value increases, the diffraction peaks corresponding to the wavelength unchanged, only the diffraction peak intensity increased, and no new diffraction peaks appears follow the sharp peak. When the x value is less than 0.08, the sample excitation and emission intensity will increase as x increases; when x is greater than 0.08, the sample excitation and emission intensity will decrease as the x value increases; when the amount of the x value is equal to 0.08 Eu^{3+} , the excitation and emission spectra of the YAG: Eu^{3+} glass reach the maximum value, the peak value correspond to the $^7\text{F}_0$ - $^5\text{L}_6$ and the $^5\text{D}_0$ - $^7\text{F}_1$ transition.

When the x value is less than 0.08, Eu^{3+} ions will enter into the stroma and replace Y^{3+} ions as electron traps. The number of luminescent centers will increase with the Eu^{3+} ions concentration increases, it will make the electron trap in electron impact ionization of luminescence centers and luminescence centers with radiation or recombination probability of luminescence centers increase. When the x value is greater than 0.08, the excitation energy will deliver to the Eu^{3+} ions. The high energy will not stop in a step and energy transfer will proceed continuously due to the energy transfer between Eu^{3+} ions is very big. This will take excitation energy far away from the absorption site, energy migration appears. When the excitation energy reach the non-radiative energy (extinction or quenching site), the system luminous efficiency will decline due to the concentration quenching [19, 20, 21].

Conclusion

The YAG: Eu³⁺ fluorescent glass was obtained firstly by synthesizing Y₃Al₅O₁₂(YAG): Eu³⁺ precursors through a simple co-precipitation method, and then mixing YAG: Eu³⁺ precursor with B₂O₃-Al₂O₃-SiO₂-Na₂O-BaO glass powder calcined at 1400°C. The content of YAG precursor and Eu³⁺ ions doped in initial materials do not affect the fluorescence excitation and emission spectra of peak wavelength, but the value of the peak wavelength; when the YAG precursor is 0.9g and amount of Eu³⁺ doped is 0.08, the fluorescence excitation spectra of glass and emission spectra of the peak intensity reach its maximum value. The fluorescence excitation peak of the YAG: Eu³⁺ fluorescence glass is at 593nm, the emission peak is located at 393nm, and they basically have the same spectral characteristics with YAG: Eu³⁺ phosphors. The YAG: Eu³⁺ fluorescence glass could be a promising material for the production of near ultraviolet chip white light-emitting diode.

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Figures

Figure 1

DTA - TGA curve of raw YAG: Eu³⁺ precursor and glass

Figure 2

XRD patterns of YAG: Eu³⁺ fluorescent glass and glass

Figure 3

Excitation spectra of fluorescent glass with different content of precursor

Figure 4

Emission spectra of fluorescent glass with different content of precursor

Figure 5

Excitation spectra of YAG fluorescence glass with different content of Eu^{3+}

Figure 6

Emission spectra of YAG fluorescence glass with different content of Eu^{3+}