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Deposition of $NaGd(WO_4)_2$:Eu^{3+}/Bi^{3+} films on glass substrates and potential applications in white light emitting diodes

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ABSTRACT

$NaGd(WO_4)_2$:Eu^{3+}/Bi^{3+} films were deposited on SiO_2 glass substrates by spin-coating. The as-prepared films were heat treated at different temperatures. The properties of films were characterized by TG-DSC, XRD, SEM and fluorescence spectrophotometer. The TG-DSC curve indicated that films began to crystallize at about 600 °C. The XRD patterns and SEM images of films annealed at 600 °C, 700 °C and 800 °C showed that a higher temperature benefits to the higher crystallinity and induces the lower thickness. Meanwhile, it was found that the revolution of spin coating influenced the morphology of films obviously. Under the excitation at 396 nm, $NaGd(WO_4)_2$:Eu^{3+}/Bi^{3+} films showed characteristic emission bands originating from $^5D_0 \rightarrow {}^7F_j$ (j = 1, 2, 3, and 4) transitions of Eu^{3+} ions. It was also found that the excitation wavelength has great effect on the emission intensity.

1. Introduction

Due to the increasing energy crisis and ecocrisis, more and more researches have focused on low carbon economy. Low carbon economy has been accepted to be one of effective economic development modes for human responding to energy and environmental risks. Several of approaches have been done to accomplish low carbon economy in fields of industry and daily life, such as the appearance of more and more zero energy buildings [1], the use of solar installations in buildings [2], the use of LED in daily [3], the use of energy-saving building materials [4], and the heat recovery in industry [5]. In daily life, white light generation is needed in room lighting, displays, monitors, and other optical devices. And white light emitting diodes (WLEDs) are the most promising white light sources [3]. WLED-based lighting has advantages of lower energy consumption, longer lifetime, higher luminous efficiency and brightness, wider operating temperature range, and better mechanical impact resistance, comparing with traditional incandescent or fluorescent lamps [6,7]. In other words, WLED can be one of attempts to accomplish low carbon economy in daily life.

It has been reported that rare earth ions doped garnet luminescence-film grown on single crystal substrates can withstand much higher power densities than powder phosphors without tube degradation [8]. The film-phosphor has uniform thickness, smoother surface and small grain size, which makes it possible to define a smaller pixel spot size to achieve a higher resolution [9]. Moreover, it demonstrates a large separation between the phosphor and the primary LED emitter (referring to as remote phosphor arrangement), which enhances a phosphorescence extraction by reducing optical power absorbed by an LED chip [10]. Generally, the remote phosphor can be obtained by fabricating a phosphor layer on a regular soda lime silicate (SLS) or SiO_2 glass substrates [11,12].

The combination of green and red emitting phosphors with a blue chip benefits to the fabrication of WLEDs with high color rendering and high efficiency [13]. In the past decades, Eu^{3+} ion is used widely as an ideal red comment because of its excellent color purity [14]. When Eu^{3+} ion presents in a non-centrosymmetric site, phosphors have dominant red emission originating from the $^5D_0 \rightarrow {}^7F_2$ transition. And the red emission intensity can be improved by co-doping Bi^{3+} ions because of an energy transfer between Eu^{3+} and Bi^{3+} ions [15–17]. Alkali rare-earth double tungstate compounds have been studied widely for the application of phosphor host [18–23]. $NaGd(WO_4)_2$, as one of members of double tungstates

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family, belongs to the tetragonal system with space group of C^6_{4h} ($I4_1/a$). As a good host for rare earth ions, $NaGd(WO_4)_2$ shows excellent thermal, hydrolytic, and chemical stability [24]. Herein, we report on the fabrication of $NaGd(WO_4)_2$:Eu^{3+}/Bi^{3+} thick films on SiO_2 glass substrates by spin-coating technique. This method has advantages of simpleness and the possibility of large-area coatings with high uniformity on various substrates [11]. The phase, microstructure and luminescent properties of the obtained phosphor-films have been characterized.

2. Experiments

All of raw materials were purchased from Aladdin and used directly without further purification. Gadolinium oxide (Gd_2O_3, 99.99%), europium oxide (Eu_2O_3, 99.99%), bismuth oxide (Bi_2O_3, 99.99%), and sodium tungstate ($Na_2WO_4{\cdot}2H_2O$, 99.99%) were used as raw materials. Deionized water was used as solvent for the synthesis of precursor solution. To obtain $A(NO_3)_3$ (A = Gd, Eu, and Bi) solution (0.5 mol L^{-1}), stoichiometric Gd_2O_3, Eu_2O_3, and Bi_2O_3 were dissolved into HNO_3 solution under heating with agitation. The precursor solution was fabricated using $GdCO_3OH$:Eu^{3+}/Bi^{3+} and $Na_2WO_4{\cdot}2H_2O$ as raw materials.

For the preparation of $GdCO_3OH$:Eu^{3+}/Bi^{3+}, 2 mL of $A(NO_3)_3$ solution was mixed with 48 mL of deionized water and stirred for about 15 min. Then, 5 g of carbamide (H_2NCONH_2, 99.5%) was added into the above solution. Subsequently, the total volume of the solution was adjusted to be 100 mL by adding appropriate deionized water. The final solution was wrapped in a beaker by polyethylene film and stirred for about 15 min. Finally, the mixed solution was heated at 80 °C for about 4 h under strong stirring. The obtained suspension was separated by centrifugation and collected after washing with deionized water for several times. The concentration of Eu^{3+} was fixed as 4 mol%. To study the influence of Bi^{3+} concentration on the luminescence of samples, samples with different concentrations of Bi^{3+} (0, 4 mol%, 8 mol%, and 12 mol%) were synthesized.

In the synthesis of $NaGd(WO_4)_2$:Eu^{3+}/Bi^{3+} precursor solution, the as-prepared $GdCO_3OH$:Eu^{3+}/Bi^{3+} was dispersed into 35 mL of deionized water and treated for about 15 min by ultrasonic. Then, 2 mmol of $Na_2WO_4{\cdot}2H_2O$ was added into the above solution. Subsequently, 2 mL of 2-methoxyethanol was added for adjusting viscosity. To keep the precursor solution stable, appropriate amount of acetylacetone ($C_5H_8O_2$, 99%) was also added into the solution. After an agitation about 30 min, the precursor solution was obtained.

The $NaGd(WO_4)_2$:Eu^{3+}/Bi^{3+} films were deposited on SiO_2 glass substrates by spin-coating. The substrates were boiled in nitric acid, rinsed with deionized water and air-dried under infrared lamp firstly. Then, the precursor solution was coated onto the substrates at 3000 RPM (revolutions per minute) for about 20 s at room temperature and dried at 300 °C for 10 min in air to eliminate the solvent and organic residue. The same spin coating procedures were repeated 12 times. Finally, the films were annealed at 600 °C, 700 °C, and 800 °C for 3 h in air. To investigate influence of rotation speed on the surface of films, different speeds (1000, 2000, 3000, and 4000 RPM) were used to deposit films.

Thermogravimetric and differential scanning calorimetry (TG-DSC) data were recorded with a thermal analysis instrument (SDT 2960, TA Instruments, New Castle, DE) at a heating rate of 10 °C min^{-1}. The X-ray diffraction (XRD) patterns of thin films were examined by a Japan RigaKu D/max-g X-ray diffractometer system with graphite monochromatized Cu Kα irradiation. The surface morphology of thin film was observed by a scanning electron microscope (SEM, JEOL JSM-6301F). The excitation and emission spectra were taken on a Hitachi F4500 fluorescent spectrophotometer equipped with a 150 W xenon lamp as the excitation source. All of measurements were carried out at room temperature.

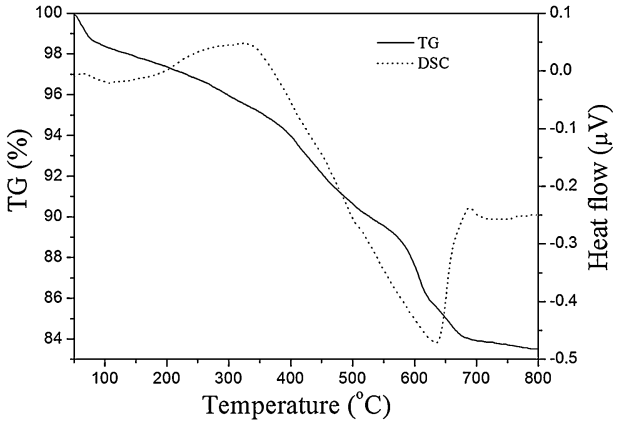

Fig. 1. TG-DSC curve of $NaGd(WO_4)_2$:0.04Eu^{3+}/0.12Bi^{3+} precursor.

3. Results and discussion

The thermal behavior of the as-prepared $NaGd(WO_4)_2$: 0.04Eu^{3+}/0.12Bi^{3+} precursor is investigated by TG-DSC measurement. The obtained TG-DSC curve is shown in Fig. 1. It can be seen from the TG curve that the weight lessens continually up to 700 °C, corresponding to the two exothermic peaks at 325 °C and 689 °C. Above 700 °C, no abrupt weight loss can be observed. Fig. 2 shows the XRD patterns of $NaGd(WO_4)_2$:0.04Eu^{3+}/0.12Bi^{3+} films annealed at 600 °C, 700 °C, and 800 °C for 3 h, respectively. After an annealing at 600 °C, the sample shows the tetragonal phase with space group of $I4_1/a$ and lattice parameter values of $a = b = 5.243$ Å, $c = 11.384$ Å, and $\alpha = \beta = \gamma = 90°$, which is well according with the JCPDS card No. 25-0829 [25]. The peaks are sharper due to the increases of annealing temperatures, which indicates the increase of crystallinity. No impurity phase can be observed in the XRD patterns. This fact implies clearly that Eu^{3+}/Bi^{3+} ions have doped into $NaGd(WO_4)_2$ host entirely and formed solid solution. Eu^{3+} and Bi^{3+} ions are expected to substitute Gd^{3+} sites, as they have same oxidation states and similar ionic radii. Likewise, only single $NaGd(WO_4)_2$ phase is observed for all of films with different doping

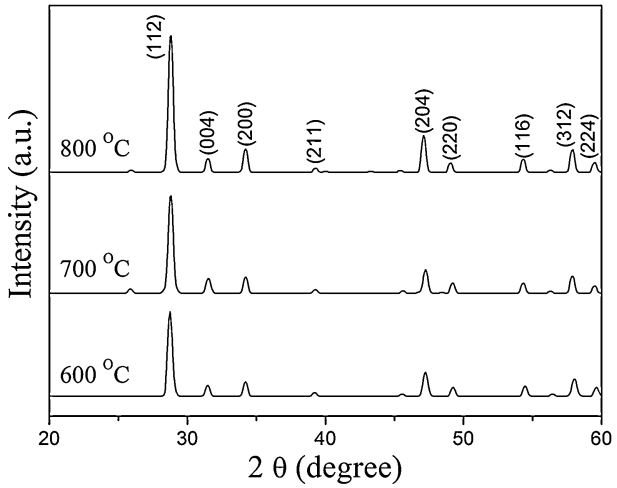

Fig. 2. XRD patterns of $NaGd(WO_4)_2$:0.04Eu^{3+}/0.12Bi^{3+} films annealed at 600 °C, 700 °C, and 800 °C for 3 h.