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Role of synthesis method and α, β-$Sr_{(2-x)}SiO_4$: xEu^{2+} phases on the photoluminescent properties of $Sr_{(1-x)}Si_2O_2N_2$: xEu^{2+} phosphors

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ABSTRACT

$SrSi_2O_2N_2$: Eu^{2+} (SSON) phosphors were prepared using two-steps synthesis method with Sr_2SiO_4: Eu^{2+} (SSO) as a precursor. In the first step, coprecipitation (CO), Pechini sol-gel (PSG), sol-gel (SG), and solid-state reaction (SS) methods were performed, whereas the second step was used SS method. The effects of the α- and β-SSO phases in the first step on the luminescence intensity, crystallite size, and quantum efficiency of SSON in the second step are investigated. The photoluminescence results of SSON show an emission spectrum band between 460 and 640 nm with green emission peaks at 530 nm. The luminescence emission intensity of SSON phosphor was increased in the order of CO, PSG, SG, and SS methods. The results indicate that increasing of β-SSO phase in the first step using a specific preparation method is an important key to obtain high-efficiency SSON phosphors for their promising application in WLEDs.

1. Introduction

Phosphor-converting white light-emitting diodes (WLEDs) have received considerable attention because of their advantages such as their low energy consumption, small bulk, non-toxicity, environmental friendliness, and long operation lifetime [1,2]. Oxynitride phosphors are notably attractive for WLEDs because of their excellent chemical, optical, mechanical, and thermal stability [3,4], which enable oxynitrides to be used in various industries including the photovoltaic, photothermal, photocatalytic, pigment, lighting and display, and optoelectronic fields [5].

Strontium oxonitridosilicate $SrSi_2O_2N_2$ (SSON) is an excellent oxynitride host material for phosphor with efficient conversion for WLEDs applications in near-UV or blue-emitting InGaN LEDs because of their thermal and chemical stability, high quantum efficiency, strong absorption in the near-UV to blue-light region, and non-toxicity [6]. One-step synthesis via conventional solid-state reaction was used to prepare Eu^{2+}-doped SSON [7,8], and two-steps synthesis was used to prepare Eu^{2+}-doped SSON using Sr_2SiO_4: Eu^{2+} (SSO) as a precursor; both steps were conducted using a conventional solid-state reaction. The crystallinity and luminescence efficiency were increased compared with one-step conventional solid-state reaction method [9]. According to the literature, the activation energy of two-steps synthesis phosphor is 408.82 kJ/mol, whereas it is 561.47 kJ/mol for one-step synthesis, which indicates that two-steps synthesis process is easier to perform and produces better crystallinity than one-step process [10]. Two-steps synthesis of SSON is shown in the chemical Eqs. (1) and (2).

$$2SrCO_3 + SiO_2 + {}^1/_2\ Eu_2O_3 \rightarrow Sr_2SiO_4{:}\ Eu^{2+} + 2CO_2\uparrow \quad (1)$$

$$Sr_2SiO_4{:}\ Eu^{2+} + Si_3N_4 \rightarrow 2SrSi_2O_2N_2{:}\ Eu^{2+} \quad (2)$$

Strontium orthosilicate Sr_2SiO_4 has two crystalline structures, as follows: α is the high-temperature form with the orthorhombic in *Pmab* (space group #62), which occurs at a temperature higher than 85 °C, and β is the low-temperature form with a monoclinic crystal system in $P2_1/c$ (space group #14), which occurs at a temperature below 85 °C [11,12]. The previous study in Ref. [9] shows that the use of SSO as a precursor to obtain SSON can improve its crystallinity and luminescence efficiency. However, the effect of the α- and β-SSO phases in the first step on the

Abbreviations: SSON, $SrSi_2O_2N_2$; SSO, Sr_2SiO_4; CO, coprecipitation; PSG, Pechini sol-gel; SG, sol-gel; SS, solid-state reaction; IQE, internal quantum efficiency; EQE, external quantum efficiency.

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photoluminescence properties of SSON in the second step has not been well discussed.

In the present study, we prepared the SSON phosphor by two-steps synthesis method using SSO as a precursor in the first step. The first-step compound was prepared using coprecipitation (CO), polymer sol-gel (PSG) [Pechini process], sol-gel (SG), and solid-state reaction (SS) methods, and the second-step compound was prepared using SS method. The emission intensity of phosphors is strongly affected by particle size and morphology. Many experimental results show that particles with uniform spherical shape of optimal size have better luminescence properties than those with irregular shapes [13]. The preparation of SSO as a precursor using different chemical methods makes it have different proportions of α and β-SSO phases and a difference in morphology and particle size, which affect the luminescence properties of SSON in the second step. We selected an Eu^{2+} content of x = 0.06 for CO, SG, and PSG methods, whereas x = 0.08 for SS method because we found that these contents have the highest emission intensities.

2. Experimental

2.1. Preparations

2.1.1. First step—synthesis of Sr_2SiO_4: xEu^{2+}

2.1.1.1. Coprecipitation method. $Sr_{(2-x)}SiO_4$: xEu^{2+} (x = 0.06) phosphor is prepared from the starting materials of $Sr(NO_3)_2$ (AR), TEOS (AR) and $Eu(NO_3)_3{\cdot}6H_2O{\cdot}Sr(NO_3)_2$ and $Eu(NO_3)_3{\cdot}6H_2O$ were dissolved in H_2O/EtOH (v:v = 5:1). The solution was stirred until the solution became clear. The silica sol solution was prepared by dissolving TEOS in an appropriate amount of HNO_3 (1 M), ethanol and water while stirring for 20 min. Then, the TEOS solution was added to the first solution while stirring until the solution became clear. Afterward, 97 mL of NH_4HCO_3 and 3 mL of NH_4OH were used as precipitating agents, which were added to the above solution with a flow rate of 5 mL/min under stirring. After aging for 24 h, the solution was filtered and rinsed with de-ionized water. The sediment was dried at 120 °C for 1 h, heated in a muffle furnace at 1000 °C for 1 h and subsequently sintered in a horizontal tube furnace at 1200 °C for 2 h under a reductive atmosphere (N_2 95%–H_2 5%) to obtain the phosphor powders.

2.1.1.2. Sol-gel method. The mixture of the TEOS solution with strontium and europium nitrate solution was placed in a water bath at 80 °C to obtain a transparent gel. The gel was dried and heated at 120 °C for 24 h to remove the water and subsequently reheated at 600 °C for 2 h. The sintering was performed at 1200 °C for 2 h in the same reductive atmosphere.

2.1.1.3. Pechini method. The polymer metal complex method was used to prepare $Sr_{(2-x)}SiO_4$: xEu^{2+} following a procedure reported elsewhere [14].

2.1.1.4. Solid-state reaction method. $Sr_{(2-x)}SiO_4$: xEu^{2+} (x = 0.08) was prepared by mixing stoichiometric amounts of $SrCO_3$ (AR), SiO_2 (4N) and Eu_2O_3 (4N) with ethanol and then uniformly grinding in a mortar. The ground mixture was then placed in an alumina crucible and heat treated for 3 h at 1400 °C in the same reductive atmosphere.

2.1.2. Second step—synthesis of $SrSi_2O_2N_2$: xEu^{2+}

The SSO phosphors obtained from the first step were used as precursors to prepare $Sr_{(1-x)}Si_2O_2N_2$: xEu^{2+} by mixing with α-Si_3N_4 (AR) and subsequently firing at 1400 °C for 4 h in the same reductive atmosphere.

2.2. Characterization

The formation phases of $Sr_{(2-x)}SiO_4$: xEu^{2+} and $Sr_{(1-x)}Si_2O_2N_2$: xEu^{2+} were characterized by X-ray diffraction XRD (Ultima IV, Rigaku, Tokyo, Japan) using CuKα radiation (λ = 1.542 Å). The PL spectra were measured using a fluorescent spectrophotometer (F7000, Hitachi, Tokyo, Japan), which was equipped with a 60 W Xenon lamp. The internal quantum efficiency (IQE) was measured at 440 nm using (FLS-980, Edinburg Instrument Ltd., Livingston, England). The morphology of the phosphor particles was observed using a scanning electron microscope (SEM TM3000, Hitachi, Tokyo, Japan). A laser particle size analyzer (LS603, OMEC Instruments Ltd., Guangdong, China) was used to determine the particle size of phosphors.

3. Results and discussion

Fig. 1 shows the XRD patterns of $Sr_{(2-x)}SiO_4$: xEu^{2+} phosphors that were prepared by several methods. Orthorhombic α-Sr_2SiO_4 phase ICDD 39-1256 and monoclinic β-Sr_2SiO_4 phase ICDD 38-0271 coexisted in the prepared samples. To determine the proportion and purity of α and β-SSO phases, two methods were used, first, Jade XRD analysis program and second, the purity of the β-phase formula [15] as shown in the following formula:

$$P_\beta = \frac{I_\beta}{I_\alpha + I_\beta} \tag{3}$$

where $P\beta$ is the purity of the β-phase, and $I\beta$ and $I\alpha$ are the integral peak intensities of (301) for β-phase in 2θ = 32.4° and (112) in 2θ = 27.2° for α-phase in the XRD patterns, respectively. These two peaks can distinguish between α- and β-phases as shown in the insets of Fig. 1. The proportions of α- and β-phases in methods 1 and 2 are shown in Table 1. The results of both methods are fairly close to each other. The lowest amounts of β-SSO phase in CO method are 4.8% and 5.52%, whereas the highest amounts of α-phase are 95.2% and 94.48%. The percentage of β-SSO phase gradually increased in PSG, SG, and SS methods, whereas the percentage of α-phase decreased. All prepared samples do not have pure α or β-phase because of the low transition temperature between the two phases, which is approximately 85 °C.

In the crystal structure of Sr_2SiO_4, there are two different strontium sites: Sr(1) with 9 coordinated oxygen and Sr(2) with 10 coordinated oxygen. In α-(SSO), the SiO_4 tetrahedron is unusually small, and the bond strength of Sr(1)—O is weak because of the

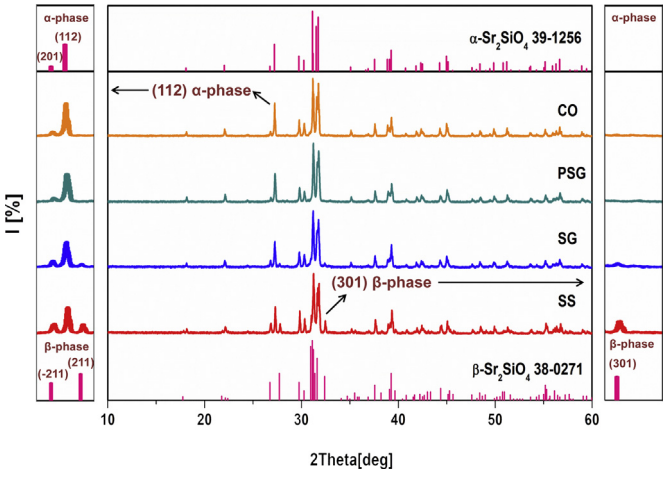

Fig. 1. XRD patterns of SSO prepared by four methods.