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Short communication

Synthesis and photoluminescent properties of $Sr_{(1-x)}Si_2O_2N_2$: xEu^{2+} phosphor prepared by polymer metal complex method for WLEDs applications

Dhia A. Hassan[a,b], Jian Xu[a], Yibin Chen[a], Langkai Li[a], Renjie Zeng[a,c,*]

[a] Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, PR China
[b] Department of Chemistry, College of Education for Pure Science, University of Basrah, Basrah 61004, Iraq
[c] Fujian Key Lab of Advanced Special Materials, Xiamen University, Xiamen 361005, PR China

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ABSTRACT

Green emitting $Sr_{(1-x)}Si_2O_2N_2$: xEu^{2+} ($x = 0, 0.02, 0.04, 0.06, 0.08$ and 0.1) phosphors were synthesized by polymer metal complex or pechini method. The XRD results confirm the formation of a pure phase at 1400 °C for 3 h. The SEM and particles size results indicate that the prepared phosphor consists of a polyhedral crystalline shape with well dispersed and the average particle size around 6.5 μm. The maximum PL intensity was found at 0.04% Eu^{2+} with a wide emission band between 460 and 640 nm and a green emission peak at 531.4 nm. The external quantum efficiency of 0.04% Eu^{2+} sample was 43.13%. The results indicate that pechini method is an alternative way and close in efficiency to the solid state method to prepare $SrSi_2O_2N_2$ phosphor with higher homogeneity and more uniform size distribution for near UV and blue region applications for white light emitting diodes WLEDs.

1. Introduction

White light emitting diodes (WLEDs) have been investigated extensively in the applications of solid state lighting such as backlighting source for liquid crystal displays, incandescent lamps and indicators due to their low operating voltage, reducing energy consumption, increasing the emission efficiency and long operation life time. It is expected to replace the conventional incandescent lamps to be considered the next generation of the lighting system [1,2]. $SrSi_2O_2N_2$ (SSON) is an excellent oxynitride host material as wavelength conversion phosphors in the WLEDs applications due to its high quantum efficiency, strong absorption in the near UV to blue-light region, good thermal and chemical stability compared to most oxide and sulfide phosphors [3].

The luminescent properties of Eu^{2+} doped SSON prepared by conventional solid state reaction have been thoroughly studied [3,4]. The results revealed poor homogeneity particles and need a high sintering temperature, therefore many alternative methods are used to obviate these problems such as, sol–gel [5], hydrothermal reaction [6], microwave reaction [3] and carbothermal reduction [7]. The chemical methods play important roles in the processing of phosphor, due to the high purity and compositional homogeneity of the produced powder with a low temperature synthesis [8,9]. Polymer metal complex or pechini method (PM) is a polymer sol–gel process suitable to produce an oxide network from molecular precursors by polymerization reaction with stable citrate/metal complexes formed [8] and well ions dispersed in the polymer network at the molecular level without precipitation; yields finer powders with a more uniform size distribution, as well as high purity, short heating time, low cost, low temperature process and its simplicity.

Many researches have been conducted to prepare $SrSi_2O_2N_2$: Eu^{2+} in a homogenous form with a small particle size, since the particle size, shape and morphology have a significant effect on photoluminescence properties of phosphors [10], The morphology of SSO was found non-uniform and have agglomeration [11,12].

Despite the difficulties to obtain nitride phosphor by PM [13]; we successfully investigated a suitable procedure by DTA–TG curves to prepare $SrSi_2O_2N_2$: Eu^{2+} phosphor using the PM for the first time. The morphology, particles size and quantum efficiency

Abbreviations: SSON, $SrSi_2O_2N_2$; PM, pechini method; SSM, solid state method; IQE, internal quantum efficiency; EQE, external quantum efficiency.

* Corresponding author at: Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, PR China.
Fax: +86 592 2183937.
E-mail addresses: dhia_hassan@yahoo.com (D.A. Hassan), rjzeng@xmu.edu.cn (R. Zeng).

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were studied and compared with solid state method SSM. The photoluminescence properties have been reported.

2. Experimental

2.1. Preparation

According to the chemical composition of $Sr_{(1-x)}Si_2O_2N_2$: xEu^{2+} (x = 0, 0.02, 0.04, 0.06, 0.08 and 0.1), The starting materials $Sr(NO_3)_2$ (Ar) and $Eu(NO_3)_3{\cdot}6H_2O$ were dissolved in the deionized water until the solution became transparent. $Si(OC_2H_5)_4$ (Ar) dissolved in appropriate amount of ethanol and water, then added to the first solution with stirring for 30 min, Si_3N_4 (Ar) was added to solution under stirring for 30 min too. Citric acid and ethylene glycol with molar ratio 2:1 were added to the solution of cations and stirring till we get a uniform mixture, then transfer to a water bath at 80 °C until the sol transform into a sticky gel, which dried at 85 °C for 10 h. Subsequently, the polymeric resin was heated at 150 °C for 3 h and 300 °C for 3 h to get a charcoal-like porous precursor then heated to 700 °C for 3 h to remove the organics and carbon and was then heated in a tube furnace at 1400 °C for 3 h under reducing atmosphere (H_2 5%-N_2 95%). The obtained powder was washed with a 10% HNO_3 to remove some impurity phases.

The same composition was also prepared by conventional solid state reaction using $Sr(CO_3)_2$ (Ar), SiO_2 (Ar), α-Si_3N_4 (Ar) and Eu_2O_3 as a starting materials which mixed by grinding and sintering at 1400 °C for 6 h in the same reduction atmosphere.

2.2. Characterization

The resultant powders were identified by X-ray diffraction (XRD, Rigaku Ultima IV) using CuKα radiation (λ = 1.542 Å). The luminescent properties were measured using a fluorescent spectrophotometer (Hitachi F7000) equipped with a 60 W Xenon lamp and an integrating sphere. A (NETZSCH STA 449F3) thermos-analyzer was conducted to record DTA–TG curves with heating speed of 10 °C/min in nitrogen atmosphere. The internal quantum efficiency (IQE) was measured at 440 nm using (Edinburg Instrument Ltd., FLS-980). The particle morphology was observed using scanning electron microscope (SEM, Hitachi TM3000). The particle size was determined by Laser particle size analyzer (LS603).

3. Results and discussion

The DTA–TG curves of the gel precursor are shown in Fig. 1. The weight loss occurred in four steps, first weight loss (2.5%) happened at 25–190 °C accompanied by an exothermic peak at 130 °C in DTA curve is attributed to the elimination of water from the gel. The significant weight loss was found in a second step (43%) between 190 and 630 °C with a sharp endothermic peak at 628 °C in a DTA curve because of the decomposition of the polymer to H_2O and CO_2. The third step at 628–930 °C, the weight loss about (11%) and the DTA shows a small peak at 865 °C which can attribute to the decomposition of starting materials intermediates via organic precursor reactions. The fourth small weight loss from 930 to 1400 °C could be assigned to remove the oxidize carbon from the decomposed organic compounds [14]. The DTA shows two peaks; first one at 1165 °C probably due to the formation of Sr_2SiO_4 phase and second at 1347 °C attributed to the crystallization of SSON phase. Depending on the above DTA–TG results, multi-heated stages were carried out to prepare SSON phosphor: 150, 300, 700 and 1400 °C.

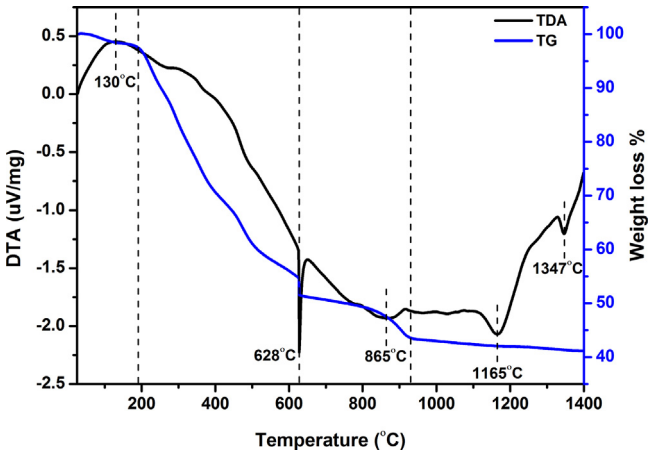

Fig. 1. The DTA–TG curves of the gel dried at 150 °C for 3 h.

Fig. 2 shows the XRD pattern of $Sr_{(1-x)}Si_2O_2N_2$: xEu^{2+} phosphors prepared by the PM at 1400 °C for 3 h. All the peaks are matched well with ICSD-172877 and proved a triclinic system with the P1(No.1) space group 15 [15], no impurity phase was present in the samples and no significant change in the host structure with doping of Eu^{2+}, indicate that the activator have been incorporated into the lattice and XRD results in agreement with DTA–TG results. The prepared phosphor is oxygen rich oxynitride phosphor because the peak in 31.69 2θ stronger than that in 25.35 2θ [3]. The morphology of the sample doped with Eu^{+2} was dispersed well and homogenous with some agglomerations as shown in SEM image Fig. 3(a), the particles have a polyhedral crystalline shape [Fig. 3(b)] and the particle size distribution with an average size of D_{50} = 6.5 μm as obtained from a particle size analyser in [Fig. 3(c)], while its about 10 μm in SSM sample as shown in Supplementary 1. The crystallinity and morphology of our samples are better than Refs. [11] and [12].

Fig. 4(a) shows the excitation and emission spectrum of Eu^{2+} doped $SrSi_2O_2N_2$ prepared by PM at room temperature, the excitation spectra monitored at λ_{em} 527 nm and emission spectra were recorded under λ_{ex} 440 nm. The emission spectrum shows a wide band from 460 to 640 nm, with a green emission peak at about 530 nm which is attributed to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+}. Fig. 4(b) shows the maximum intensity at Eu^{2+} = 0.04 at% at 531.4 nm after that the intensity decreases due to the concentration quenching. The peak excitation wavelengths are almost same and originated from the 4f–5d transition of the doped Eu^{2+} ions,

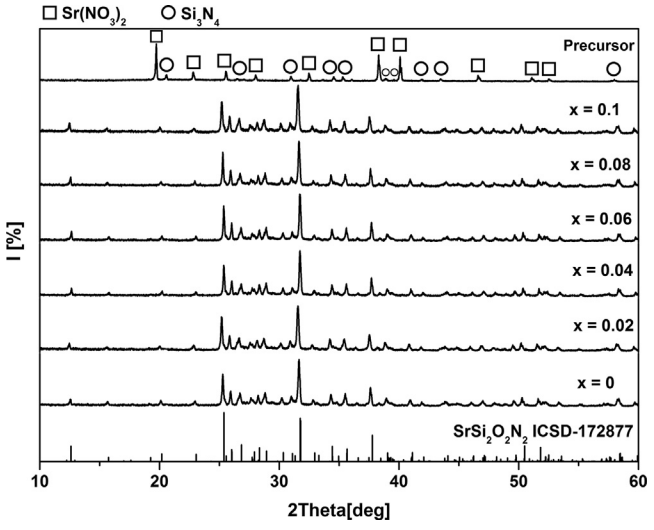

Fig. 2. The XRD pattern of the precursor and (SSON) with different Eu^{2+} content prepared by (PM) at 1400 °C for 3 h.