Optical Materials 38 (2014) 242–247

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Photoluminescence of $CaAlSiN_3:Eu^{2+}$-based fine red-emitting phosphors synthesized by carbothermal reduction and nitridation method

Shuxing Li [a,b], Xia Peng [a,b], Xuejian Liu [a,*], Zhengren Huang [a]

[a] Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China
[b] University of the Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:
Received 14 August 2014
Received in revised form 9 October 2014
Accepted 22 October 2014
Available online 8 November 2014

Keywords:
$CaAlSiN_3:Eu^{2+}$
Red phosphor
Crystal phase
Luminescence property

ABSTRACT

In this research, we have presented the synthesis and characterization of the various $Ca_{1-x}Eu_xAl_{0.76}Si_{1.18}N_3$ ($x = 0.01 \sim 0.1$) red-emitting phosphors, which were successfully prepared by carbothermal reduction and nitridation (CTRN) method without the strict needs of high pressure. Here, raw materials were $CaCO_3$, AlN, Si_3N_4, Eu_2O_3, and C. In particular, C was considered as efficient and robust reducing agent. The influences of reaction temperature, holding time, C content, and Eu^{2+} concentration were investigated in the crystal phase compositions and photoluminescence properties of the as-prepared phosphors. Importantly, $CaAlSiN_3:Eu^{2+}$-based red phosphors with interesting properties were obtained with reaction temperature at 1600 °C for 4 h by atmospheric N_2–10%H_2 pressure, and the C/O ratio of 1.5:1, respectively. The emission peak positions of as-prepared phosphors were red-shifted from 607 nm to 654 nm with Eu^{2+} concentration from 1 mol% to 10 mol%. Meanwhile the highest luminescence intensity was achieved with 2 mol% of Eu^{2+} concentration, which showed high external quantum efficiency up to 71%. Combining the phosphor blend of green-emitting β-sialon:Eu^{2+}, yellow-emitting Ca-α-sialon:Eu^{2+}, and red-emitting $Ca_{0.98}Eu_{0.02}Al_{0.76}Si_{1.18}N_3$ with a blue LED (light emitting diodes), warm white LED can be generated, yielding the color rendering index (Ra) of 93 at correlated color temperature (CCT) of 3295 K. These results indicate that $CaAlSiN_3:Eu^{2+}$-based red-emitting phosphors prepared by facile CTRN are highly promising candidates for warm white LEDs.

1. Introduction

In recent years, rare earth doped (oxy)nitrides phosphors have been attracting much attention because of their nontoxicity, excellent thermal stability, and high absorption and conversion efficiency from near-UV to visible spectral region [1]. Typically, they are AlN:Eu^{2+} [2–4], and $LaSi_3N_5:Ce^{3+}$ [5] blue-emitting phosphors, β-SiAlON:Eu^{2+} [6–9], $CaSi_2O_2N_2:Eu^{2+}$ [10,11], and γ-AlON:Mn^{2+} [12] green-emitting phosphors, Ca-α-SiAlON:Eu^{2+} [13,14], and $Y_3Si_6N_{11}:Ce^{3+}$ [15] yellow-emitting phosphors, and $SrAlSi_4N_7:Eu^{2+}$ [16], $M_2Si_5N_8:Eu^{2+}$ (M = Ca, Sr, Ba) [17–19], and $CaAlSiN_3:Eu^{2+}$ [20–23] red-emitting phosphors. Among these (oxy)nitrides, $CaAlSiN_3:Eu^{2+}$ red-emitting phosphors have been used as key materials for high color rendering index (CRI) and low correlated color temperature (CCT) solid illumination parts, which satisfy the requirements of medical and architectural lighting fields. Both excitation and emission bands of $CaAlSiN_3:Eu^{2+}$ showed very low energies due to the contributions by a combination of strong crystal-field splitting of the 5d states of Eu^{2+} ions and high covalence (nephelauxetic effect), especially for the first nearest coordination of Eu–N [24].

Up to now, various preparation methods for $CaAlSiN_3:Eu^{2+}$ red-emitting phosphors have been reported. It included traditional high temperature solid state reaction (SSR) [19], spark plasma sintering (SPS) [25] with Ca_3N_2–AlN–Si_3N_4 as raw materials, self-propagating high-temperature synthesis (SHS) [22], direct nitridation [26], and ammonothermal synthesis [21,27] based on $Ca_{1-x}Eu_xAlSi$ alloy. However, raw materials of all the mentioned methods were air-sensitive and oxygen-free metal nitrides or active metals, especially for expensive and deliquescent Ca_3N_2. Consequently, all the procedures before sintering must be taken in a glove box filled with N_2 to avoid oxidation. Additionally, crushing and classification process must be taken on the phosphors prepared at relative high temperature (⩾1800 °C) and pressure (⩾0.9 MPa). At the same time, impurities would be inevitably introduced during crushing and classification process. Ammonothermal synthesis by nitridation of (Ca, Eu)AlSi alloy in supercritical ammonia (100 MPa) could never be industrially applicable because of extremely high pressure for use. Recently, Suehiro and co-workers [23] reported the synthesis of $CaAlSiN_3:Eu^{2+}$ phosphors by gas reduction nitridation (GRN)

---

[*] Corresponding author at: Dingxi Road 1295, Shanghai, China. Tel.: +86 21 52414220; fax: +86 21 52413903.

E-mail address: xjliu@mail.sic.ac.cn (X. Liu).

http://dx.doi.org/10.1016/j.optmat.2014.10.039
0925-3467/

method with complex process, however, the obtained product contained impurities of AlN and unreacted CaO. By comparison with mentioned methods, carbothermal reduction and nitridation (CTRN) method possesses the high advantage of relative low reaction temperature, cheap raw materials, and simple processing. At present, there are few reports of the synthesis of $CaAlSiN_3:Eu^{2+}$ red phosphors through CTRN method except for the research by Kim et al. [28,29] with hazardous $CaCN_2$ as calcium and carbon sources. In this research, nominal compositions of $Ca_{1-x}Eu_xAl_{0.76}Si_{1.18}N_3$ ($x = 0.01 \sim 0.1$) red phosphors were synthesized with stable and inexpensive $CaCO_3$ as calcium source at relatively low temperature and by atmospheric pressure. The main effects of reaction temperature, holding time, C content and Eu^{2+} concentration on crystal phase compositions and photoluminescence properties were investigated in order to develop low-cost and high-quality $CaAlSiN_3:Eu^{2+}$-based red-emitting phosphors.

2. Experimental

2.1. Synthesis

Nominal compositions of $Ca_{1-x}Eu_xAl_{0.76}Si_{1.18}N_3$ ($x = 0.01$, 0.02, 0.03, 0.05, 0.08, and 0.1) red-emitting phosphors were synthesized according to the stoichiometric ratio. The raw materials of $CaCO_3$ (99.99%), AlN (Tokuyama, H-Grade), α-Si_3N_4 (UBE, E-10), Eu_2O_3 (99.99%), and C powder (99.95%) were homogeneously mixed in a silicon nitride mortar. The resultant mixture was heated in atmospheric N_2 at a constant flow rate of 200 mL/min at 850 °C for 1 h to decompose $CaCO_3$ completely. Then, H_2 gas was flowed inside the horizontal tube furnace by 200 mL/min N_2 to 20 mL/min H_2 gas mixture to guarantee the complete reduction of Eu^{3+} to Eu^{2+}. Next, the temperature was increased to 1550–1650 °C, and maintained for 1–6 h. Finally, the fired samples were ground finely and prepared for measurements.

2.2. Characterization

The crystal phases of sintered samples were determined by X-ray diffraction (XRD) (Bruker D8 Advanced) with Cu $K\alpha_1$ radiation ($\lambda = 0.15406$ nm) operating at 40 kV/40 mA with a step size of 0.02° and a scan speed of 5° min^{-1}. Electron micrograph of the typical sample was obtained by field-emission scanning electron microscope (Hitachi S-4800). Partial elemental analysis of the phosphors was performed using C measurement device (SICMMC-222) for C content, and O and N analyzer (LECO, Model TC600) for O and N content, respectively. The photoluminescence spectrum and quantum efficiency of powder phosphors were determined by fluorescence spectrophotometer (Jobin Yvon, Fluoromax-4) with 150W Xe lamp as excitation source. The quantum efficiency was estimated using an integrating sphere unit (Jobin Yvon, F-3029) with a monochromatic source of 460 nm. For the temperature-dependent photoluminescence measurement, the powder sample was loaded in a sample cavity and then heated to the desired temperature by a high-temperature fluorescence controller (Tianjin Orient KOJI Co., Ltd., TAP-02). The sample was kept for 10 min to guarantee a uniform temperature both on the surface and in the interior of the sample. The optical properties of as-fabricated white LED was investigated by a UV–VIS-near IR Spectrophoto Colorimeter (PMS-80) with an integrating sphere under forward-bias current of 20 mA at room temperature.

3. Results and discussion

3.1. Reaction temperature

Fig. 1 showed typical X-ray diffraction (XRD) patterns of $Ca_{0.98}Eu_{0.02}Al_{0.76}Si_{1.18}N_3$ powders synthesized at 1550 °C, 1600 °C, and 1650 °C with C/O ratio of 1.5:1 and the same holding time for 4 h, respectively. As $CaCO_3$ was decomposed completely into CaO above 1000 °C, the O of C/O referred to oxygen element in CaO and Eu_2O_3 oxides. We suggested that the powders synthesized at temperature of 1550 °C contained a small amount of impurity phases Ca_2SiO_4 and unreacted C. The impurity phases of Ca_2SiO_4 and unreacted C gradually disappeared with an increasing temperature, and the $CaAlSiN_3$ phase (JCPDS 39-0747) and a very small amount of $CaAl_{0.54}Si_{1.38}N_3$ phase (ICSD 161796) [24] were formed without impurities at temperatures of 1600 °C and 1650 °C in Fig. 1.

The excitation and emission spectra of $Ca_{0.98}Eu_{0.02}Al_{0.76}Si_{1.18}N_3$ phosphors synthesized at different temperatures were presented in Fig. 2. Each phosphor showed a broad excitation spectra from 250 to 600 nm, matching effectively with UV (~380 nm) and (or) blue (~450 nm) LED chips. The strong orange–red emission spectra centered at about 630 nm were attributed to the characteristics of $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ions [20–23]. The product synthesized at temperature of 1550 °C became gray because of the existence of unreacted C, which absorbed visible spectra intensively, leading to the large reduction of luminescence intensity. The phosphor heated at 1600 °C showed the best luminescence whose full width at half maximum (FWHM) of the emission band was about 100 nm. However, when we increased the reaction temperature up to 1650 °C, the luminescence intensity decreased, the reason for which was unclear in this case.

3.2. Holding time

Under the atmosphere of C and H_2 strong reducing agents, CaO and Eu_2O_3 were reduced to corresponding metals, and at the same time, they were nitrogenized and N needed to diffuse into metal particles in order to react completely. However, in the solid–solid reaction process N diffused very slowly into metal particles [2]. At the same time, low reactivity and small self-diffusion coefficient of silicon nitride and aluminum nitride also slowed the solid–solid diffusion process, but diffusion process was the rate-determining step in the whole reaction process [18]. Thus, the holding time was an important factor to produce pure crystal phase with good crystallization. As a result, the effect of holding time on the most typical XRD patterns of $Ca_{0.98}Eu_{0.02}Al_{0.76}Si_{1.18}N_3$ phosphors synthesized at 1600 °C with C/O ratio of 1.5:1 was shown in Fig. 3. The intensity of diffraction peaks of unreacted C decreased without eliminating completely with holding time increasing from 1 h to 2 h, indicating that the C content decreased with longer holding

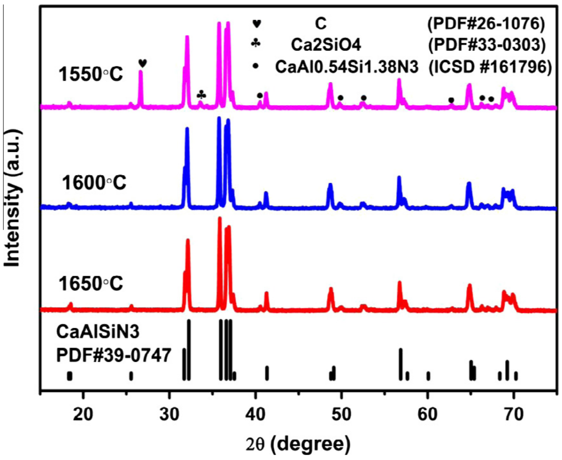

Fig. 1. X-ray diffraction patterns of $Ca_{0.98}Eu_{0.02}Al_{0.76}Si_{1.18}N_3$ powders synthesized at different temperatures.