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Effect of starting composition and post-anneal on the structure and luminescence properties of Eu-doped Ca-α-SiAlON phosphors prepared by combustion synthesis

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Abstract: Eu-doped Ca-α-SiAlON yellow phosphors, with the compositions $Ca_{0.72}Eu_{0.08}Si_{9.56}Al_{2.44}O_{0.84}N_{15.16}$, were prepared by a highly efficient combustion synthesis method. By optimizing the starting compositions of reactants and choosing appropriate post-annealing conditions, phase-pure, uniform and fine Ca-α-sialon:Eu^{2+} phosphors possessing the particle size ranging ~3–5 μm, and good luminescence properties with an intense emission band that peaks at 592 nm under n-UV or blue light excitation were obtained. The results indicated that combustion synthesis method was an energy efficient, time saving and low cost way to prepare Ca-α-SiAlON phosphors by controlling the mass ratio of comburents. A combination with post-annealing treatment was desired for further increase of the properties of Ca-α-SiAlON phosphors.

Keywords: combustion synthesis; Ca-α-SiAlON:Eu^{2+}; photoluminescence; post-anneal; rare earths

White light-emitting diodes (LEDs) have attracted significant attention recently as a light source for the next-generation general illumination and the automotive forward lighting applications, due to their advantages such as energy saving, long lifetime, environmental friendly, low maintenance cost and good safety[1,2].

In order to obtain white LEDs with better color rendering ability, higher efficiency and longer lifetime, SiAlON-based nitride have emerged as a promising candidate. The highly condensed $SiN(O)_4$-based networks guarantee high conversion efficiency, low thermal quenching, as well as extraordinary chemical and thermal stability in the near-UV and blue spectral range[3–6].

Generally, SiAlON-based nitride phosphors are synthesized by the conventional solid-state reaction (SSR) method of high-purity α-Si_3N_4, AlN and other constituent metal oxide or nitride reactants under pressured N_2 atmosphere of 1–10 MPa at estimated 1600–2000 °C for several hours, even days, followed by post synthesis grinding step to pulverize crude reaction products[6–15]. This process requires the use of expensive raw materials, a high-temperature and N_2-pressure furnace with long processing time, and complex post synthesis grinding steps, unarguably leading to low manufacturability. Therefore, a highly efficient and cheap method of preparing SiAlON-based nitride phosphors needs to be explored for practical industrial application.

In this paper, Eu-doped Ca-α-SiAlON phosphors were prepared by highly efficient combustion synthesis method. Combustion synthesis, also termed self-propagating high-temperature synthesis (SHS), takes advantage of the self-sustaining merit from highly exothermic reactions, and hence, enjoys the benefits of low energy consumption, short processing time, and simple facilities[16–21]. In addition, this method provides advantages like cheaper raw materials, lower energy consumption, and loose products easier for pulverization, making combustion synthesis a potential method of preparing SiAlON phosphors for industrial applications.

In 2008, Zhou et al.[22] succeeded in synthesizing β-SiAlON:Eu^{2+} phosphor by a highly efficient combustion synthesis method. But so far, there has been no detailed report on preparing α-SiAlON phosphors by combustion synthesis. We are eager to find out whether Eu^{2+} can be incorporated into the α-SiAlON lattice to serve as effective luminescence activators during the rapid combustion synthesis process and how to improve the photoluminescence property of α-SiAlON by regulating and controlling reaction parameters.

1 Experimental

1.1 Experimental design

α-$Ca_{(m/2-x)}Eu_xSi_{12-m-n}Al_{m+n}O_nN_{16-n}$ phosphors were pre-

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pared by combustion synthesis according to the following general reaction:

$$\frac{a(12-m-n)}{3+a}\mathrm{Si}+\frac{12-m-n}{3+a}\alpha\text{-}\mathrm{Si_3N_4}+\frac{b(4m+n+x)}{3+3b}+\mathrm{Al}+\frac{4m+n+x}{3+3b}\mathrm{AlN}+\frac{m-2x}{2}\mathrm{CaO}+\frac{2n-m-x}{6}\mathrm{Al_2O_3}+\frac{x}{2}\mathrm{Eu_2O_3}\xrightarrow{\mathrm{N_2\ gas}}\alpha\text{-}\mathrm{Ca}_{(\frac{m}{2}-x)}\mathrm{Eu}_x\mathrm{Si}_{12-m-n}\mathrm{Al}_{m+n}\mathrm{O}_n\mathrm{N}_{16-n} \quad (1)$$

In Eq. (1), all the parameters: m, n, a, b, x determine the ratio of initial raw materials, which affect the procedure of combustion synthesis and the properties of products. i. m represents the number of Al–N bonds substituting Si–N bonds; n represents the number of Al–O bonds substituting Si–N bonds. m and n combined determine the chemical ratio of the product[23]. ii. a is the molar ratio of raw silicon to α-Si_3N_4 and b is the molar ratio of raw aluminum to AlN. Both a & b decide on the ratio of combustible in the reaction system and then affect the energy and temperature of the whole reaction[24,25]. iii. x represents the doping ratio of Eu^{2+}, that is the concentration of activator in synthetic product.

In the first step, Eu^{2+}-doped Ca-α-SiAlON (Ca-α-SiAlON:Eu^{2+}) phosphors with the compositions of $Ca_{0.72}Eu_{0.08}Si_{9.56}Al_{2.44}O_{0.84}N_{15.16}$ (m=1.6, n=0.84, x=0.08) were prepared by combustion synthesis.

Presented by Xie et al.[8], all α-SiAlONs, starting at low Eu^{2+} concentration, the emission intensity rises to a maximum at a Eu^{2+} concentration of x=0.075 and falls again steadily to a minimum at x=0.25, which can be explained by concentration quenching, in reference to that, x was fixed at 0.08 in our experiments. Meanwhile, the stable point of m=1.6, n=0.84 in the phase diagram was chosen so that the oxygen element in the system can be totally supplied by reactants Eu_2O_3 and CaO, without adding Al_2O_3 for extra oxygen supply, control parameters of the experiments can be simplified.

Therefore, the combustion synthesis reaction can be expressed as the following Eq. (2):

$$\frac{9.56a}{3+a}\mathrm{Si}+\frac{9.56}{3+a}\alpha\text{-}\mathrm{Si_3N_4}+\frac{2.44b}{1+b}+\mathrm{Al}+\frac{2.44}{1+b}\mathrm{AlN}+0.72\mathrm{CaO}+0.04\mathrm{Eu_2O_3}\xrightarrow{\mathrm{N_2\ gas}}\alpha\text{-}\mathrm{Ca_{0.72}Eu_{0.08}Si_{9.56}Al_{2.44}O_{0.84}N_{15.16}} \quad (2)$$

During the reacting process, the systematic energy mainly came from the nitriding combustion of reactants Si and Al. In order to investigate the influences of the mass ratio of comburents (Si & Al) in the starting reactants on the properties of synthesized products, the starting powders were weighed according to the compositions listed in Table 1. The total mass of reactants for each experiments was 50 g, changing 'a' (molar ratio of Si/α-Si_3N_4) values from 1.921, 1.375, 2.601, 4.614 to 8.526 while keeping 'b' (molar ratio of Al/AlN) value as 4.000 gave the five starting compositions designated as M-30, M-35, M-40, M-50 and M-60. For sample M-30, the mass ratio of comburents (Si & Al) in the starting reactants is 30%, while the amount of added silicon powder increased in the sequence of M-35 to M-40 to M-50 to M-60. All these five starting compositions were designed to synthesize a phosphor with a nominal composition of α-$Ca_{0.72}Eu_{0.08}Si_{9.56}Al_{2.44}O_{0.84}N_{15.16}$.

Table 1 Starting compositions for synthesizing α-$Ca_{0.72}Eu_{0.08}Si_{9.56}Al_{2.44}O_{0.84}N_{15.16}$ phosphor (Mass/g)

	M-30	M-35	M-40	M-50	M-60
a	**1.921**	**1.375**	**2.601**	**4.614**	**8.526**
b	4.000	4.000	4.000	4.000	4.000
Eu_2O_3	1.386	1.424	1.463	1.540	1.616
α-Si_3N_4	27.675	24.97	22.27	16.86	11.46
Si	**9.814**	**12.17**	**14.53**	**19.24**	**23.95**
CaO	3.970	4.080	4.190	4.410	4.630
AlN	1.970	2.024	2.079	2.188	2.297
Al	5.186	5.330	5.473	5.761	6.048
Si & Al	**30%**	**35%**	**40%**	**50%**	**60%**

* 'Si & Al' represents the mass ratio of comburents (Si & Al) in the starting reactants

1.2 Materials

Commercially available powders of Si, AlN (Tokuyama Corp., Type F, Japan), α-Si_3N_4 (TX-Q, Tomley Hi-tech New Materials Co., Ltd., Yantai, China), Eu_2O_3 (Grirem Advanced Materials Co., Ltd., Beijing, China), CaO and Al (Sinopharm Chemical Reagent Co., Ltd., China) were used as starting materials.

1.3 Combustion synthesis of Ca-α-sialon:Eu^{2+} phosphors and post-annealing

The starting powders were mixed in anhydrous ethanol using a nylon jar with α-Si_3N_4 balls by a planetary mill for 3 h. After vacuum drying in a drying oven for 12 h and sieving, the mixed reactants were put into a steely reaction vessel covered by carbon felt with a length of 200 mm, a width of 75 mm and a height of 150 mm. Moderate amount of titanium powder, serving as igniter, was then put on the mixed reactants in the reaction vessel, while a tungsten filament was set closely to the titanium powder. After that, the reaction vessel was placed into a reaction chamber. After 3 times of evacuation, high purity N_2 gas was filled into the reaction chamber till 3.25 MPa. By passing a 20 A electric current through the tungsten filament, the combustion reaction was ignited and then preceded rapidly within a few minutes.

Post-annealing (at 1600, 1700 and 1800 °C respectively in a nitrogen pressure of 0.9 MPa for 3 h) was applied to the combusted products from sample M-35, in order to reveal the effect of high-temperature thermal treatment on the structure and luminescence properties.