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Cost-effective synthesis of Ca-α-sialon:Eu^{2+} phosphors by a direct silicon nitridation route

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Abstract

The direct silicon nitridation method was used to synthesize Ca-α-sialon:Eu^{2+} phosphors. From a low cost $CaCO_3$–AlF_3–Si mixture, pure α-sialon phase was produced at a low temperature of 1250 °C. The crystallinity of the obtained phosphors can be markedly improved by increasing the firing temperature or post-annealing. Solid–gas reactions occur easily, according to thermodynamic analysis, leading to loss of silicon and enhancing the replacement of Si–N bonds by Al–N bonds. The produced Ca-α-sialon:Eu^{2+} phosphors feature high purity, uniform and discrete particle morphology with a particle size of 1–2 μm and good luminescence properties with a yellow emission that peaks at 580 nm under n-UV or blue light excitation.

Keywords: A. Sintering; C. Optical properties; D. Nitrides; D. Sialon

1. Introduction

In the development of white light-emitting diodes (LEDs), in particular for general illumination applications, rare-earth doped (oxo)nitridosilicates have emerged as suitable candidate phosphors. The highly condensed SiN_4-based networks guarantee their high conversion efficiency, long excitation wavelength, low thermal quenching, and extraordinary chemical and thermal stability in the n-UV and blue spectral range [1–5]. As a typical representative of (oxo)nitridosilicates, α-sialons are solid solutions in the M–Si–Al–O–N system, which have structures derived from α-Si_3N_4 with the general formula $M_x^{v+}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$, where $x = m/v$ and M is the stabilizing cation (Li, Ca, Mg, and rare earths) [6]. Rare earth doped α-sialon phosphors have recently attracted considerable attention as wavelength-conversion materials for white LEDs [7,8].

Nevertheless, the conventional solid-state reaction (SSR) approach for synthesizing Ca-α-sialon phosphors has disadvantages in terms of powder mixing, high cost, and low yields in industrial level production, because the starting powders must be expensive high-purity nitride powders, such as Si_3N_4 and $Si(NH_2)_2$. Therefore, many efforts have been made to search for other routes of synthesis [9–12]. Since silicon powder is easy to purify without inducing any redundant agent, in this study we propose a cost-effective direct silicon nitridation (DSN) method, which omits the complicated pre-synthesis process or synthesizing (oxo)nitridosilicate phosphors [13], to produce Ca-α-sialon:Eu^{2+} ($Ca_{0.95}Eu_{0.05}Si_9Al_3ON_{15}$) phosphor. The effect of starting powders, synthesis temperatures, and post-annealing treatment was investigated.

2. Materials and methods

Commercially available powders of $CaCO_3$, Si, Al_2O_3, $Al(NO_3)_3·9H_2O$, $AlF_3·3H_2O$, $Al(OH)_3$ (Sinopharm Co. Ltd., Shanghai, China), Si_3N_4 (SN-E10, Ube Industries, Japan), AlN (Grade F, Tokuyama Soda Co., Japan), and Eu_2O_3 (99.99%, Yuelong Co. Ltd., Shanghai, China) were used. Six different compositions from Y0 to Y5 were prepared. For each particular composition, the starting powders were different with regards

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Table 1
Starting powders used for the samples Y0–Y5.

Sample	Y0	Y1	Y2	Y3	Y4	Y5
Al source	AlN	AlN	$Al(NO_3)_3 \cdot 9H_2O$	$AlF_3 \cdot 3H_2O$	$Al(OH)_3$	Al_2O_3
Si source	Si_3N_4	Si	Si	Si	Si	Si

to the powder used as a source of Al and the powder used as a source of Si, as shown in Table 1. Powder mixtures, with the weights of stoichiometry of $Ca_{0.95}Eu_{0.05}Si_9Al_3ON_{15}$, were thoroughly mixed by ball milling in a Si_3N_4 jar with Si_3N_4 balls in ethanol for 3 h. The dried powders were transferred into BN crucibles and fired at 1250–1400 °C for 4 h in a horizontal tube furnace in an NH_3 atmosphere with a flow rate of 0.3 L/min. Post-annealing (at 1600 °C for 2 h) was applied to some of the powders produced. Y0 was synthesized at 1600 °C following the SSR method for comparison.

The crystallographic analysis was carried by X-ray diffraction (Philips PW 1700 X-ray diffractometer, using Cu $K\alpha_1$ radiation, $\lambda = 0.154056$ nm). An internal standard of KCl was added to reduce errors. The photoluminescence (PL) spectra were measured at room temperature by a fluorescent spectrophotometer (F-4600, Hitachi Ltd., Japan, with a 200 W Xe-lamp as an excitation source). The morphology of the powders was observed with a scanning electron microscope (JEOL JSM-6390 equipped with a field emission gun at an acceleration voltage of 20.0 kV).

3. Results and discussion

Due to the low melting point of silicon (1413 °C), the process of synthesis by the DSN method must be carried out at temperatures below 1450 °C. The diffractograms of the produced powders of samples Y1–Y5 prepared at 1400 °C are plotted in Fig. 1. Samples Y2, Y4, and Y5 contained α-sialon and β-sialon along with some unavoidable aluminates. The compounds of $Al(NO_3)_3 \cdot 9H_2O$ of Y2 and $Al(OH)_3$ of Y4 should decompose to active Al_2O_3 during firing. So, liquid-phase should form in these three samples at a lower temperature, which corresponds to the ternary eutectic point in the $CaO–Al_2O_3–SiO_2$ system. This will lead to the formation of β-sialon, because gaseous nitridation promotes the growth of α-Si_3N_4 crystals while the liquid reaction leads to the growth of β-Si_3N_4 crystals [14]. In sample Y5, there are some remains of unreacted silicon, which can be attributed to the low reactivity of Al_2O_3 powder at 1400 °C and the insulation of the reactants due to the presence of the liquid phase.

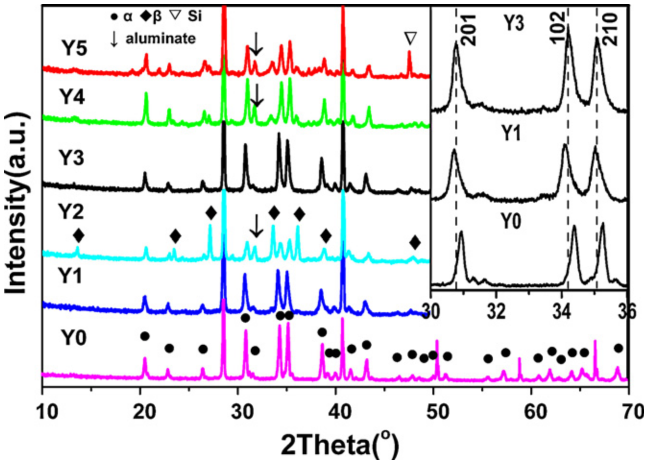

Fig. 1. X-ray diffractograms of the powders of Y1–Y5 prepared by DSN method and Y0 prepared by SSR method. The peaks at 28.494°, 40.735°, 50.461° and 66.775° are the reference peaks of cubic KCl. The inset shows the shift of the peaks in the samples Y0, Y1 and Y3 (α: JCPDS 33-0261; β: JCPDS 48-1165; Si: JCPDS 75-0589).

Pure α-sialon phase was obtained only in samples Y1 and Y3. Sample Y3 had better crystallinity, attributing to the lower reactivity of AlN at 1400 °C. With respect to Y0, the diffraction peaks of Y1 and Y3 obviously shift to lower angles (inset of Fig. 1). The expansion of the lattices can be attributed to the reactions

$$4AlF_3(s) + 3Si(s) + 4NH_3(g) \rightarrow 4AlN(s) + 3SiF_4(g) + 6H_2(g)$$
$$\Delta_r G_m^\theta \text{ (kJ/mol)} = 108.532 - 0.619436T \quad (1)$$

and

$$Si(s) + CO_2(g) \rightarrow SiO(g) + CO(g)$$
$$\Delta_r G_m^\theta \text{ (kJ/mol)} = 182.579 - 0.176617T, \quad (2)$$

which release SiF_4 and SiO gases, respectively. Both the reactions are thermodynamically favorable under the experimental conditions, for $\Delta_r G_m^\theta = -943.363$ kJ/mol for Eq. (1) and $\Delta_r G_m^\theta = -117.343$ kJ/mol for Eq. (2) at 1400 °C. (All the reference data are obtained from NIST-JANAF Thermochemical Tables Fourth Edition.) As a result, more, longer bonds of Al–N (0.187 nm) and Al–O (0.175 nm) will replace the Si–N bonds (0.174 nm), leading to an expansion of the lattice. The powders of the Y3 composition have slightly smaller lattice parameters than Y1, probably because of the higher oxygen content due to the partial dehydration of $AlF_3 \cdot 3H_2O$ during heating.

The synthesis of Ca-α-sialon phosphors by the solid state reaction method or by the carbothermal reduction nitridation

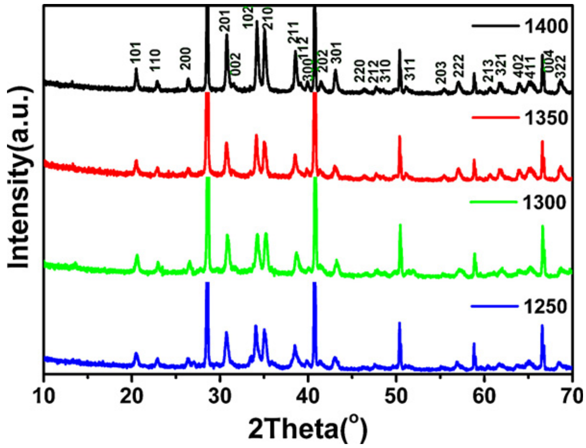

Fig. 2. X-ray diffractograms of Y3 samples fired at 1250–1400 °C for 4 h. The identification of the X-ray peaks for α-sialon was made with the JCPDS 33-0261.

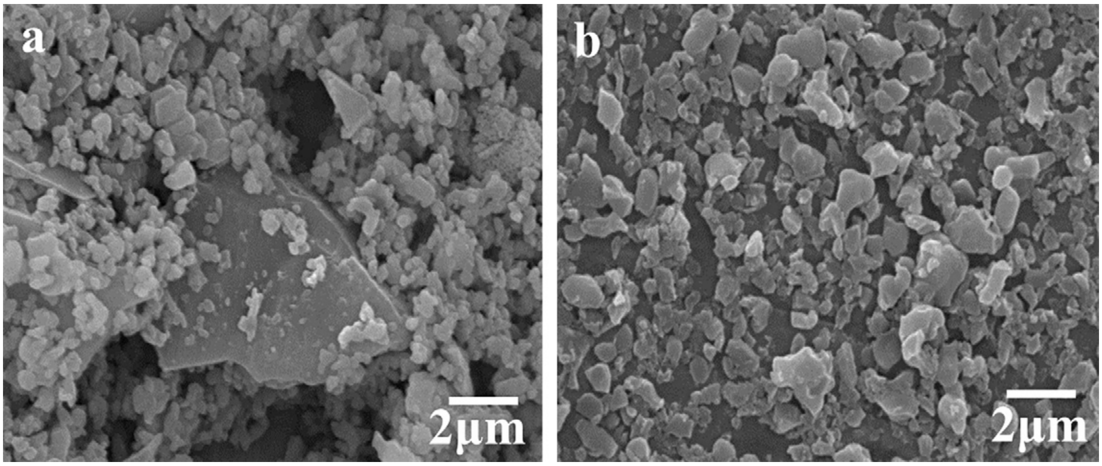

Fig. 3. SEM images of Y3 (a) the starting powder and (b) the product powders at 1400 °C.

method often occurs at high temperatures between 1500 °C and 2000 °C [15]. The gas reduction nitridation method decreases the preparation temperature to 1450 °C [9]. Since all the starting powders used here had high reactivity, the DSN method showed a much lower formation temperature. As shown in Fig. 2, the α-sialon phase was formed at a low temperature of 1250 °C and the crystallinity increased significantly with increasing firing temperature. A strong silicon flow phenomenon, which might greatly hinder the reaction process, would take place above 1413 °C, so no higher temperature was tested. Hence, it is suggested that 1400 °C is the appropriate temperature to synthesize Ca-α-sialon:Eu^{2+} phosphors by this method using active and cheaper $AlF_3 \cdot 3H_2O$ as a reactant. The SEM images of Y3 in Fig. 3 show that the starting powders contained big silicon blocks but the phosphor powders produced have particles with uniform discrete shape with a size of 1–2 μm. Silicon is considered to be transferred in the gaseous state during the nitridation process. Hence, the large silicon particles eventually disappear and the particle size and morphology of the original silicon powder have no influence on the final product. This result also suggests that the gaseous reaction is advantageous for the formation of the α-sialon structure.

To reveal the effect of high-temperature thermal treatment, the obtained Y3 phosphors were fired at 1600 °C for 2 h. Fig. 4 shows XRD patterns of this powder and Fig. 5 shows the corresponding PL spectra before and after post-annealing. In both cases, α-sialon is the only phase recorded. This suggests that the post-annealing thermal treatment has a negligible influence on phase composition. However, the greater sharpness and intensity of the diffraction peaks of the thermally treated (annealed) phosphors suggests a higher crystallinity and a better compositional homogeneity compared to the as-produced powders. The excitation spectrum has two broad bands that peak at ~300 nm and ~410 nm, which are both associated with transitions from the lower energy level of the $4f^7$ configuration to the energy levels of the $4f^65d$ configuration of Eu^{2+}, instead of the adsorption of the host lattice. The host adsorption band of Ca-α-sialon is still a debated issue, but the concept of the host band locating at wavelengths below 220 nm is generally accepted [16,17]. The excitation bands increase after post-heating, especially the one around 400 nm. The emission intensity about 580 nm is enhanced significantly while the weaker emission about 480 nm nearly disappears, which is likely due to the improvement of the Eu^{2+} local environment. During the initial step of the nitridation process,

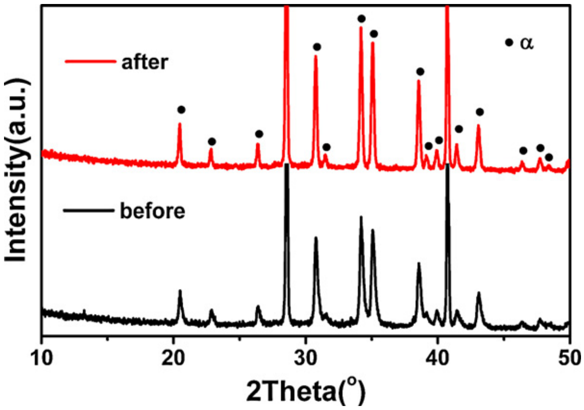

Fig. 4. X-ray diffractograms of Y3 phosphors before and after post-annealing (α: JCPDS 33-0261).

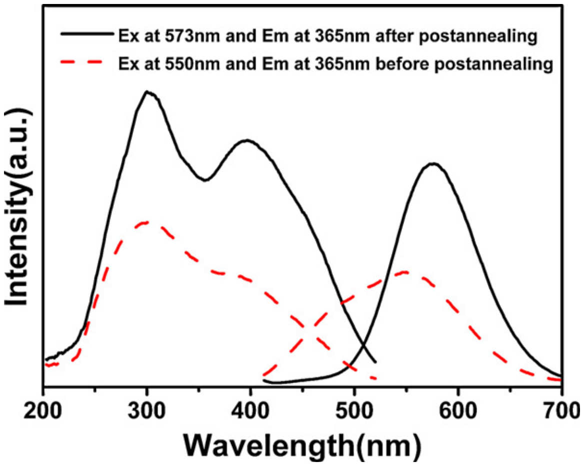

Fig. 5. PL spectra of Y3 phosphors before and after post-annealing.

Eu^{2+} can enter the structure of α-sialon, but the surroundings may still remain partially imperfect. Most oxygen atoms are probably concentrated around Eu^{2+}, leading to an asymmetric distribution of the oxygen content. Accordingly, the Eu^{2+} environment can be effectively improved by post-heat treatment.

4. Conclusions

Well-dispersed Ca-α-sialon:Eu^{2+} phosphors have been successfully synthesized at low temperatures by a direct silicon nitridation method using cost-effective starting powders of $CaCO_3$–AlF_3–Si. Their luminescence properties can be improved greatly by a second heat treatment at high temperature. The experimental results suggest that the direct silicon nitridation route is suitable for synthesizing a wide range of (oxo)nitridosilicate phosphors with improved homogeneity and good photoluminescence efficiency.

Acknowledgments

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