Fine yellow $\alpha$-SiAlON:Eu phosphors for white LEDs prepared by the gas-reduction–nitridation method

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Abstract

Yellow-emitting $\alpha$-SiAlON:Eu$^{2+}$ phosphors were synthesized by the gas reduction and nitridation of a homogeneous oxide precursor in a CaO–Al$_2$O$_3$–SiO$_2$–Eu$_2$O$_3$ system at 1400–1450°C using an NH$_3$–CH$_4$ mixture gas as a reduction–nitridation agent. The precursor was prepared by a sol–gel process using a low-cost nitrate, tetraethyl orthosilicate and citric acid as the starting materials. The effects of reaction parameters such as heating rate, temperature, holding time and CH$_4$ content on the composition, microstructure and photoluminescence of the prepared powders were investigated. Nearly single-phase $\alpha$-SiAlON was successfully synthesized by the one-step gas reduction and nitridation without the need for post-annealing at a higher temperature. The prepared powders consisted of relatively well-dispersed and uniform crystals with a hexagonal shape. The photoluminescence spectra of Eu-doped Ca-$\alpha$-SiAlON phosphors excited by near-ultraviolet or blue light showed a broad, yellow emission band at 500–700 nm, which agrees well with that obtained from phosphors prepared by the conventional solid-state reaction.

Keywords: Gas-reduction nitridation; Sol–gel process; $\alpha$-SiAlON:Eu; Phosphor; Photoluminescence; White light-emitting diodes (LEDs)

1. Introduction

$\alpha$-SiAlONs are solid solution compounds of hexagonal $\alpha$-Si$_3$N$_4$ and have an overall composition given by the formula

$$\text{Me}^{p+}x\text{Si}_{12-(m+n)}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n},$$

where $m$(Si–N) is replaced by $m$(Al–N), and $n$(Si–N) is replaced by $n$(Al–O). The charge discrepancy introduced by the former substitution is counterbalanced by the introduction of metal ions Me$^{p+}$ with $x = m/p$ (p is the valency of the metal cation Me). There are two interstitial sites per unit cell in the $\alpha$-Si$_3$N$_4$ structure that can be occupied by Me$^{p+}$ metal ions, which limits the maximum value of $x$ to 2 in formula (1), because each unit cell contains four formula units. The Me elements that have been reported to stabilize the $\alpha$-SiAlON structure are Li, Mg, Ca, Y and the rare-earth metals except for Ce, La, Pr and Eu [1–4]. Generally, it is impossible to stabilize the $\alpha$-SiAlON structure for rare-earth metals with a large ionic size such as Eu$^{2+}$ and Ce$^{3+}$, but it is possible if they are codoped with calcium [5,6]. Moreover, the prepared Ca-$\alpha$-SiAlON:Eu phosphors show strong absorption in the UV–visible spectral region, exhibit intense yellow emission from 570 to 600 nm, and are promising wavelength-conversion phosphors for white light-emitting diodes (LEDs) when coupled with a blue GaN-based chip [7,8]. Thus, $\alpha$-SiAlON has been investigated extensively as a host material for phosphors in recent years.

Generally, $\alpha$-SiAlON is prepared from compositions in the Si$_3$N$_4$–AlN–Me$_2$O$_y$ system by a solid-state reaction sintering reaction, which usually requires high-purity nitrides as the starting materials and a high sintering temperature (i.e., 1700–2000°C). Moreover, the synthesized powders consist of hard agglomerates due to the high-temperature sintering. To make fine powders, it is essential to pulverize the as-synthesized powders, which can easily damage the particle surfaces. Therefore, attempts have been made to find alternative synthesis routes. Previous
work has shown that α-SiAlON powders can be prepared from oxide precursors by simultaneous carbothermal reduction and nitridation (CRN) in a flow of nitrogen gas [9–12]. However, except for the report of Mitomo et al. [10], there have been few papers on the synthesis of pure α-SiAlON powders by this process. These synthesized powders always contain a mixture of α-, β-SiAlON and other compounds. In addition, the CRN process may easily cause carbon contamination and the concurrent formation of SiC, which is disadvantageous to their optical applications as phosphors.

Recently, gas reduction nitridation (GRN) has been developed as a new process for preparing fine nitride powders [13–16]. The significant advantage of this process is that the nitride can be formed in a single-step process by a thermodynamically favorable gas–solid reaction between ammonia and the oxide precursor. Thus, the original particle morphology of the starting materials may be retained. Suehiro [17] applied this method to a multi-component CaO–Al2O3–SiO2 system to synthesize Ca-α-SiAlON powders using amorphous SiO2 as a source material (the source materials of Ca and Al were not mentioned in this report). However, the resultant powders calcined at 1400–1500 °C for 4 h consisted of a small amount of β-SiAlON and AlN.

The aim of this work is to prepare Eu2+-doped Ca-α-SiAlON phosphors by GRN using a NH3–CH4 mixture gas as a reduction–nitridation agent and to study the effect of processing parameters on the powder characteristics. The oxide precursor was prepared by a sol–gel process, which is a relatively easy and economical method of forming uniform and high-quality stoichiometric phosphors, particularly those containing Si. Tetraethyl orthosilicate (TEOS) was used instead of amorphous SiO2 as the Si source. Organic citric acid was used as a chelating agent to form a stable complex with metal ions to retain the compositional homogeneity. The photoluminescence properties of the Ca-α-SiAlON:Eu phosphors prepared by this method were reported and compared with those synthesized by a solid-state reaction.

2. Experimental

Aluminum nitrate (Al(NO3)3·9H2O, purity >99.99%), calcium carbonate (CaCO3, >99.99%), europium oxide (Eu2O3, >99.99%), TEOS (C8H20O4Si, >98%), nitric acid (HNO3, analytical grade), citric acid (C6H8O7, analytical grade), ethanol (C2H5OH, purity >99.99%), nitric acid (HNO3, analytical grade), citric acid (C6H8O7, analytical grade), ethanol (C2H5OH, analytical grade) and deionized water were used as starting materials in the present work. A homogeneous mixture of the Ca–Eu–Al–Si–O system with a target composition of Cα0.925Eu0.075 α0.925Eu0.075 Si9Al3ON15 (m = 2, n = 1 and Eu = 7.5 mol%) was prepared by a sol–gel process. Stoichiometric Eu2O3 and CaCO3 powders were firstly dissolved in nitric acid to form a nitrate solution. After they completely dissolved, stoichiometric aluminum nitrate and TEOS, which had been dissolved in the ethanol, were added to the resultant nitrate solution with an appropriate dosage of citric acid. The mole ratio of aluminum nitrate to citrate was 3:3.08. Then, the mixed solution was heated to about 80 °C and continuously stirred using a magnetic agitator for several hours. Upon removal of the excess water and ethanol, a transparent sol was formed. Then, further heating and constant stirring, the sol transformed into a transparent sticky gel. After that, the gel was dried at 200 °C for 4 h to obtain xerogel, which was then milled and placed in a boron nitride boat. The boat was then loaded into an alumina tubular furnace. Finally, the powders were heated to 1350–1450 °C for 4–10 h at various heating rates in a flow of NH3–CH4 (0–1.5 vol.%) mixture gas and cooled in the furnace in a flow of NH3 gas.

The phase products of the synthesized powders were identified by X-ray powder diffraction (XRD, RINT2000) at 40 kV and 40 mA using Cu Kα radiation (λ = 1.5406 Å). The powder morphology was investigated by field-emission scanning electron microscopy (FESEM, JEOL-840A). The diffusive reflection spectra were recorded using a UV–vis spectrophotometer with an integrating sphere (JASCO, Ubest V-560). The reflection spectrum of Spectralon was used for calibration (the reflectivity is nearly 100% in the range of 200–900 nm). The photoluminescence spectra of the phosphors were measured at room temperature using a fluorescent spectrophotometer (F-4500, Hitachi Ltd., Japan) with a 150 W Ushio xenon short arc lamp.

3. Results and discussion

3.1. Effect of heating rate

Fig. 1 shows XRD patterns of the precursor and product powders calcined at 1450 °C for 4 h with the heating rate varying from 200 to 500 °C/h in an NH3–1.0 vol.% CH4 atmosphere.
atmosphere. Note that after drying, the resultant precursors were amorphous, and no obvious diffraction peaks were observed. In the subsequent calcining process, the heating rate significantly affected the final reaction products. The sample calcined at a heating rate of 500 °C/h exhibited complete nitridation while consisting of a considerable amount of β-SiAlON in addition to the main crystalline phase of α-SiAlON. When the heating rate decreased from 500 to 400 and 300 °C/h, the α phase content markedly increased and the β phase content decreased. At a heating rate of 200 °C/h, the product powders consisted of a nearly pure α-SiAlON phase, and the β-SiAlON phase almost disappeared. However, a small amount of AlN formed in this case. All the results clearly indicate that a slow heating rate is more beneficial to the formation of α-SiAlON during the GRN process. If the heating rate is too fast, there is insufficient time for CH₄ to react with the oxygen in the system. As a result, the oxide system reaches the reaction temperature in more oxygen-rich compositions, which leads to the excess formation of the liquid phase, which in turn promotes the formation of β-SiAlON. This is consistent with the results of Suehiro et al. [17]. In the following experiments, the heating rate was fixed at 200 °C/h.

3.2. Effects of firing temperature and holding time

Generally, reaction products are very sensitive to firing temperature and holding time, which are the two main factors determining thermodynamic activity. This is also true for the present work. Fig. 2 gives XRD patterns of the reaction products calcined at 1350–1450 °C for different holding times in the NH₃–1.0 vol.% CH₄ mixture gas. The crystalline phases of the sample fired at 1350 °C for 4 h were the main α-SiAlON, β-SiAlON, AlN and a small amount of Si₂N₂O. Si₂N₂O was formed at low temperatures and during the early reaction stages. Its amount gradually decreased and disappeared above a certain temperature and holding time. Simultaneously, the content of the α phase increased and that of the β phase decreased with increasing temperature and holding time. However, the product obtained after calcining at 1350 °C for 20 h still contained a small amount of the β phase. At the same time, a small amount of AlN was also formed as a byproduct. When the temperature was elevated to 1400 °C, the products obtained for a holding time of 10 h only consisted of a single α phase except for a small amount of AlN. No β-SiAlON was formed. Moreover, the holding time required for the completion of the reaction decreased markedly with increasing processing temperature, from 10 h at 1400 °C to 4 h at 1450 °C, indicating that increasing the temperature or prolonging the holding time can accelerate the GRN reactions and promote the formation of α-SiAlON. The effect of the temperature is more marked than that of the holding time. The range of the molten phase in the CaO–SiO₂–Al₂O₃ system is expected to be wide at >1350 °C [18]; thus, a liquid phase might be

![Fig. 2. XRD patterns of the powders calcined at (a) 1350 °C, (b) 1400 °C and (c) 1450 °C for different holding times in an NH₃–1.0 vol.% CH₄ mixture gas.]
present during heating at 1350–1450 °C. The formation of \( \alpha \)-SiAlON may be due to the dissolution of oxides, \( \text{Si}_2\text{N}_2\text{O} \) and \( \beta \)-SiAlON, into the liquid and reprecipitation as \( \alpha \)-SiAlON [10]. As can be seen in Fig. 2, AlN always forms as a minor byproduct regardless of the existence of \( \beta \)-SiAlON, and the amount increases with increasing temperature or holding time. This also happened in the CRN reaction system [9]. As stated above, during the preparation of \( \alpha \)-SiAlON using the oxides as the starting materials, maybe a certain amount of liquid phase was formed. That is to say, the actual composition of the prepared \( \alpha \)-SiAlON deviates from its theoretical composition [17]. The actual value of \( m \) is less than 2, which leads to the reduced solubility of Al in the as-prepared \( \alpha \)-SiAlON powders. As a result, the redundant Al forms AlN. Additionally, the identification of AlN by XRD is difficult if it coexists with \( \beta \)-SiAlON because its diffraction lines at \( 2\theta = 33.24° \) and 36.04° almost overlap with the peaks of \( \beta \)-SiAlON at \( 2\theta = 33.46° \) and 36.04°. Thus, in this case, we can only identify AlN from the diffraction line at 59.40°. It is noteworthy that nearly single-phase \( \alpha \)-SiAlON powders containing only a small amount of AlN were successfully synthesized at 1400–1450 °C for 4–10 h by a one-step reaction in the current GRN process. In contrast with the previous reports [10,17], the as-prepared powders do not require post-annealing at a higher temperature and the \( \beta \) phase is completely suppressed.

SEM images of the precursor and the heat-treated powders are shown in Fig. 3. The precursor had a nonuniform and highly agglomerated morphology because of using organic citric acid as a chelating agent. The powders prepared at 1400 °C for 10 h consisted of relatively well-dispersed and uniform crystals with a hexagonal shape. The grain size was about 400–500 nm. However, the morphology of the powders prepared at 1450 °C for 4 h was irregular, although the grain size decreased to 200–300 nm, which maybe is caused by the agglomeration of the precursor and the shorter holding time. It seems that a shorter holding time at a higher reaction temperature is more advantageous to obtaining finer particles.

3.3. Effect of CH\(_4\) content

\( \text{CH}_4 \) acts as a reducing medium during the GRN process, similar to the role of carbon in the CRN process. Therefore, \( \text{CH}_4 \) plays a strong determining role in the phases of the final products, and the amount of \( \text{CH}_4 \) affects the reaction mechanism and reaction time. Fig. 4 shows the effect of the \( \text{CH}_4 \) content on the phase composition of the powders synthesized at 1450 °C for 4 h. When the content of \( \text{CH}_4 \) was less than 1.0 vol.%, the obtained product always included a certain amount of the \( \beta \) phase, indicating that the amount of \( \text{CH}_4 \) was insufficient to completely reduce the oxides. As a result, \( \beta \)-SiAlON, an oxygen-enriched product, was formed. Upon increasing the content of \( \text{CH}_4 \) in the reaction gas to 1.0 vol.%, single-phase \( \alpha \)-SiAlON was mainly formed as well as a small amount of AlN.
AlN. SiC was detected instead of AlN if the content of CH\textsubscript{4} exceeded 1.5 vol.%, which suggests that excess CH\textsubscript{4} promotes the formation of SiC. Fig. 5 shows the UV–visible diffuse-reflectance spectra of the powders for various CH\textsubscript{4} contents. In every sample, the diffuse-reflectance spectrum was almost flat in the visible wavelength region of 600–800 nm, whereas the absolute value of reflectance varied from sample to sample. The diffuse reflectance of the as-prepared powders slightly decreased from 94% to 90% and 85% with increasing CH\textsubscript{4} content from 0 to 0.5 and 1.0 vol.%, respectively. However, the sample with the CH\textsubscript{4} content of 1.5 vol.% exhibited a much lower reflectance of 65%. At the same time, the color of the sample became gray, which indicates that the sample prepared using excess CH\textsubscript{4} consists of a larger amount of carbon. Additionally, the absorption band at 300–500 nm is caused by the doped Eu\textsuperscript{2+}, which can also be observed in the excitation spectrum, shown in Fig. 6.

3.4. Photoluminescence properties of Ca-\textsubscript{3}SiAlON:Eu\textsuperscript{2+} phosphors

The photoluminescence spectra of the as-prepared Ca-\textsubscript{3}SiAlON:Eu phosphors are shown in Fig. 6. The excitation spectrum monitored at 581 or 590 nm covers a broad range of 250–500 nm, which consists of two broad bands centered at 305 and 400 nm, respectively. These two excitation bands correspond to the 4f\textsuperscript{7}→4f\textsuperscript{6}5d transition absorption of Eu\textsuperscript{2+} [6–8,17]. Upon 400 nm excitation, the emission of Eu\textsuperscript{2+} displays a broad band in the range of 500–700 nm, which results in yellow emission. The broad emission band is ascribed to the allowed 4f\textsuperscript{6}5d→4f\textsuperscript{7} transition of Eu\textsuperscript{2+}. Moreover, it is clear that the sample can also be excited efficiently in the blue-light region (420–470 nm). These emission characteristics indicate that Ca-\textsubscript{3}SiAlON:Eu phosphors are promising down conversion yellow materials for solid-state lighting utilizing GaN-based excitation in the near-UV or blue-light region. These results agree well with those reported in the earlier works [6–8,17]. In addition, as can be seen in the emission spectra, the emission intensity increases and the emission band shows a slight blueshift with the increase in processing temperature, which may reflect the differences in particle morphology, size and composition of the host lattice. This phenomenon was also reported in Ref. [17]. Further analysis of the particle size and chemical composition of as-prepared \textsubscript{3}SiAlON is underway, and will be reported elsewhere.

4. Conclusions

Fine, submicron Eu-doped Ca-\textsubscript{3}SiAlON phosphors were successfully synthesized by the gas reduction and nitridation of a homogeneous oxide precursor of CaO–Al\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2}–Eu\textsubscript{2}O\textsubscript{3} prepared by a sol–gel process using a low-cost nitrate, tetraethyl orthosilicate and citric acid as the starting materials. The reduction and nitridation
reaction was completed at temperatures as low as 1400–1450 °C for 4–10 h at a heating rate of 200 °C/h in a flow of NH₃–CH₄ (1.0 vol.%) mixture gas without the need for post-annealing at a higher temperature. The product was mainly single-phase α-SiAlON. The prepared powders consisted of relatively well-dispersed and uniform crystals with a hexagonal shape. The photoluminescence spectra of the phosphors showed a broad, yellow emission band at 500–700 nm when excited by near-ultraviolet or blue light, which agrees well with that obtained from phosphors prepared by the conventional solid-state reaction.

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