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Luminescence properties of nitrogen-rich Ca-SiAlON:Eu²⁺ phosphors prepared by freeze-drying assisted combustion synthesis

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Abstract: Nitrogen-rich Eu²⁺-doped Ca- α -SiAlON phosphors (Ca_{m/2-x}Si_{12-m-n}Al_{m+n}O_nN_{16-n-x}Eu) were synthesized by a freeze-drying assisted combustion synthesis (CS) route. Fast-synthesized products with high purity and uniform particle morphology were confirmed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The analysis of lattice parameters by comparison with empirical equations showed that the as-prepared phosphors had low oxygen content. A series of samples were prepared according to the stoichiometry of Ca_{m/2-0.08}Si_{12-m}Al_mN_{16-0.08}Eu for further research. The influences of m value on the luminescence properties were investigated in detail. As m increased, a redshift phenomenon was observed in both the excitation and emission spectra. First-principle electronic structure calculations showed that the 3d energy level of Ca played an important role in the occurrence of the redshift phenomenon.

Keywords: freeze-drying; combustion synthesis; phosphors powder; fluorescence spectra; first-principle calculation

1. Introduction

In recent years, white light-emitting diodes (WLEDs) have shown strong competitiveness in the lighting market owing to their outstanding features such as their energy-saving ability, compactness, long service life, and good chromaticity. Phosphors, which are used for light conversion, are one of the major components of WLEDs [1–2]. Due to their excellent performance, including remarkable thermal and chemical stability, high luminescence efficiency, as well as reduced thermal quenching, (oxy)nitride phosphors have been considered as an important alternative to conventional phosphors [3–5]. Ca- α -SiAlON has been considered as one of the most promising (oxy)nitride phosphor matrices. In 2002, rare-earth-doped Ca- α -SiAlON phosphor was investigated for the first time by Xie *et al.* [6], and further studies have proved that it is a very promising yellow phosphor for WLEDs when packed and exhibits a wide absorption band covering from ultraviolet to blue region [5,7–8]. Because of the nephelauxetic effect and anion polarizability, the α -SiAlON:Eu²⁺ with the lowest possible oxygen content (nitrogen-rich SiAlON) has garnered great attention and may exhibit excellent photoluminescence properties, including

longer wavelength emission and good thermal quench properties [9–10].

Over the years, different methods have been developed to prepare the (oxy)nitride phosphors, such as a solid-state reaction (SSR) route [11–13], gas reduction, nitridation [14], and direct nitridation [15]. The SSR method is the most common method for the industrial production of (oxy)nitride phosphors. SiAlON phosphors have been synthesized by firing the fully mixed raw materials of Si₃N₄, Al₂O₃, and AlN powders in a gastight synthetic furnace at 1600–2000°C under 0.5–1 MPa N₂ atmosphere [16]. Each of these methods has its advantages considering the production scale and product quality [16]. However, most of these conventional methods generally utilize costly raw materials and require long synthesis time and expensive equipment, which significantly increases the production costs of Ca-SiAlON phosphors. Consequently, developing a cheaper yet highly productive route for the fabrication of Ca-SiAlON phosphors is of great value for widespread use.

The combustion synthesis (CS) method has been extensively explored for the fabrication of (oxy)nitride phosphors, owing to its advantages of having a fast reaction time, simple process, and high productivity [17–19]. In 2008, Zhou *et al.*

[20] reported the preparation of β -SiAlON phosphors by the CS method for the first time. Afterward, some experimental studies have been successfully carried out for the fabrication of α -SiAlON phosphors by the same method [21–22]. The CS method has been demonstrated for the effective and feasible production of SiAlON phosphors, but there are still several challenges and unstable factors. The questions of how to increase the packing uniformity of the raw materials and improve the permeation of nitrogen in the reaction are especially important research topics for the CS method. Recently, we reported a novel freeze-drying assisted CS method for the fabrication of nitrogen-rich SiAlON phosphors, which provided a possible solution to these problems [10].

In the present work, a modified freeze-drying assisted CS strategy was examined for the fabrication of a series of nitrogen-rich Eu^{2+} -doped Ca- α -SiAlON phosphors, which made this method more effective and productive. Phase compositions and particle morphology, as well as luminescence properties, were characterized in detail. Furthermore, a redshift phenomenon due to an increased m value (composition parameter m of $\text{Ca}_{m/2-x}\text{Si}_{12-m-n}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n-x}\text{Eu}$) was found in the emission spectra. To further elucidate the underlying mechanism, first-principle electronic structure calculations were performed.

2. Experimental

2.1. Sample preparation

The freeze-drying assisted CS method was adopted for the preparation of the nitrogen-rich Ca- α -SiAlON:Eu²⁺ phosphors. A series of compositions were designed according to

the general formula $\text{Ca}_{m/2-x}\text{Si}_{12-m-n}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n-x}\text{Eu}$, in which n and m denote the numbers of Al–O bonds and Al–N bonds substituting Si–N bonds, respectively, in each unit cell and x denotes the doping concentration of Eu^{2+} . The x value and n value were fixed at 0.08 and 0, respectively (if we ignore a small number of rare earth oxides as raw materials). Different m values were set between 1.50 and 3.93, which were 1.50, 2.00, 2.50, 2.93, 3.18, 3.43, 3.68, and 3.93. The raw materials consisted of α - Si_3N_4 (99.9wt%, Shanghai Aladdin, China), AlN (99.9wt%, Shanghai Aladdin, China), Eu_2O_3 (99.99wt%, Beijing HWRK, China), Ca_3N_2 (99wt%, Desummet Ceramic, China), and Al and Si (99.9wt%, Shanghai Aladdin, China).

The raw materials were mixed with 0.5wt% polyvinyl butyral adhesive and 80vol% tert-butyl alcohol (TBA) to form a series of TBA-based slurries. These operations should be kept away from water to avoid a reaction between water and Ca_3N_2 . All slurries were mixed by a high-speed blunger with an agitation rate of 2000 r/min for 5 min in a nitrogen atmosphere. The evenly dispersed slurry was poured into a cylindrical polyethylene mold and sealed with waterproof rubber. Then, the whole object was immersed in refrigerant (around -40°C) for 10 min. The TBA solvent rapidly froze. Then, we removed the seal rubber and the mold, and obtained a cylindrical frozen sample. At the end of this step, the frozen sample was placed into a vacuum chamber that was connected to a refrigeration thermotank. In this process, the solidified TBA slowly sublimated, and a void was left in its place. Hence, the remaining raw materials formed a porous structure (as shown in Fig. 1).

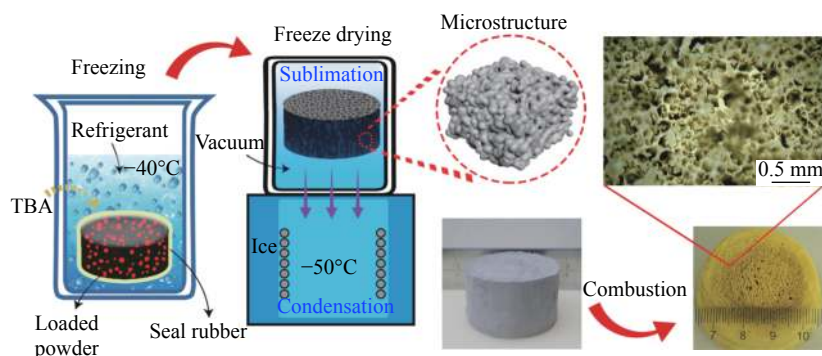


Fig. 1. Experimental method of the freeze-drying assisted combustion synthesis route and the pore structure in the as-synthesized sample.

The porous green body was quickly transferred into an airtight steely reaction chamber. A tungsten wire was pierced into the titanium powder block, which was placed on the side of the porous body. The chamber was pumped with high purity nitrogen until the pressure reached 3 MPa. By heating the tungsten wire with an electric current of 200 A, the heating agent was ignited, and a huge amount of heat was released,

thus successfully igniting the combustion reaction. The whole combustion process lasted for about 2 min, and the reactant was converted into orangish-yellow α -SiAlON phosphors.

2.2. Characterization

The phase component and lattice structure of Ca- α -SiAlON products were studied by powder X-ray diffraction

(XRD) with a D8 Focus instrument (Bruker, Germany). The lattice parameters were further analyzed using Rietveld refinement technology with the TOPAS program. The photoluminescence spectrum was investigated using an F-7000 Hitachi fluorescent spectrophotometer equipped with a 150-W Xe lamp.

3. Results and discussion

A series of Ca- α -SiAlON:Eu²⁺ phosphors with different m values were prepared by the freeze-drying assisted CS method. In previous studies, a relatively high N₂ pressure (≥ 5 MPa) or active diluents (NH₄Cl or NH₄F) have been frequently applied to promote the nitridation of reactants [22–23]. In the present work, a loosely packed green body with well-interconnected pores and high porosity was pre-

pared (as shown in Fig. 1), which provided adequate pores for better gas permeation and thus ensured thorough nitridation under a comparatively lower N₂ pressure (3 MPa) without any active diluent. By comparison, the mixed reactant powders were directly and gently stocked in the crucible to ensure the penetration path of nitrogen during the customary CS process. This way, controlling the uniformity, stacking density, and porosity of the green body of reactant powders is difficult, which can have a significant impact on the synthesis of high-quality (oxy)nitride phosphors.

The XRD results of the powders that were prepared with varying m values are shown in Fig. 2(a), where the peak positions of single α -SiAlON phases are labeled. All the obtained samples matched well with the index of α -SiAlON diffraction data (PDF card No. 48-1586), and no significant impurities were detected in the as-prepared samples.

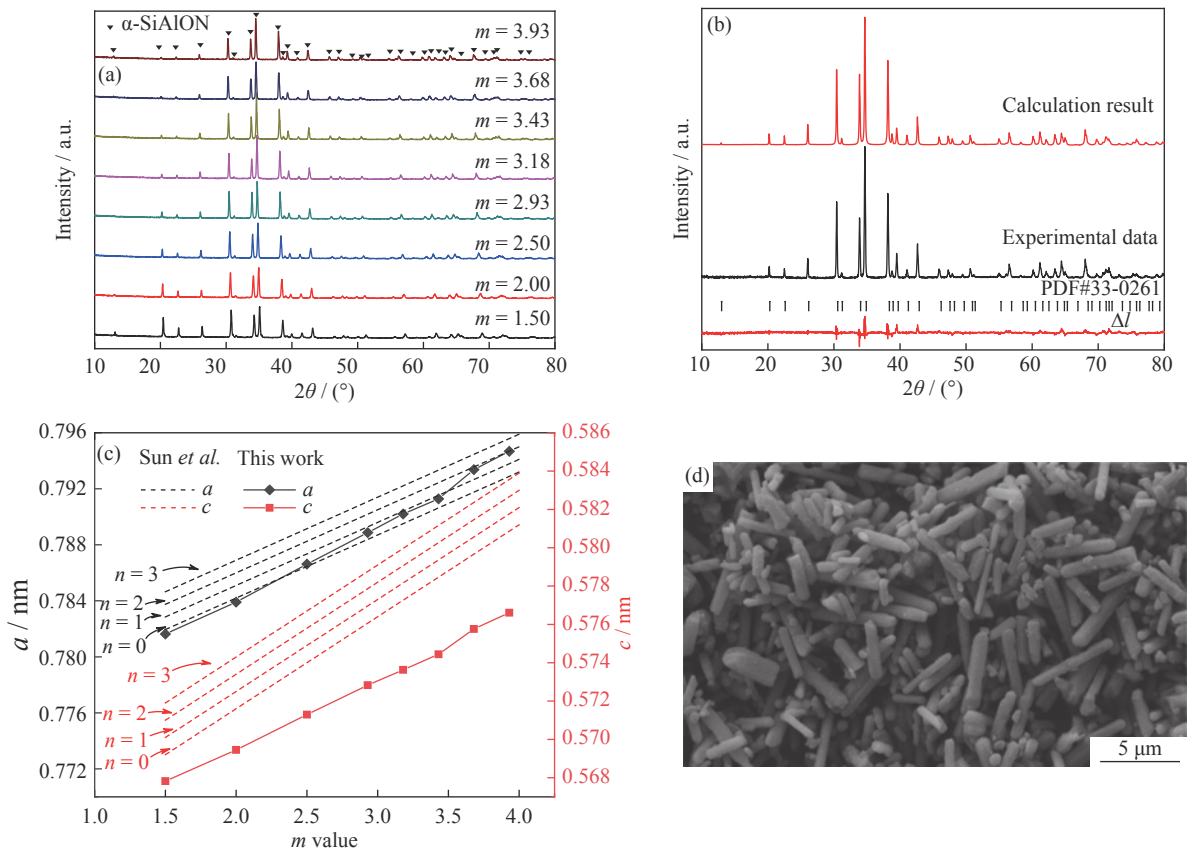


Fig. 2. (a) XRD data of the samples with different m values prepared by freeze-drying assisted combustion synthesis method. (b) Detailed analysis of the XRD result of a typical sample with $m = 3.18$, including Rietveld calculation results and experimental data as well as intensity differences (Δ) between calculation and experimental data. (c) Correlation between lattice parameters (a , c) and the number of Al-N bond in each unit cell (m value); the dashed lines are plotted according to the equations proposed by Sun et al. [24]. (d) SEM micrographs of the synthesized Ca-SiAlON:Eu²⁺ phosphor with $m = 3.18$.

Additionally, the Rietveld refinement was carried out based on the space group $P31c$ for further analysis of the lattice parameters. A typical Rietveld refinement calculation result of the sample with $m = 3.18$ is shown in Fig. 2(b). The

refinement converged to expected factor $R_{\text{exp}} = 6.67\%$ and weighted profile factor $R_{\text{wp}} = 10.37$. According to the Rietveld refinement calculation results, the lattice parameter a increased from 0.78173 to 0.79461 nm, and c increased from

0.56788 to 0.57656 nm, with increasing m values, as shown in Fig. 2(c). Previous works have revealed that the composition parameter m and oxygen content (n value) have a significant linear correlation with the lattice parameters of rare-earth-doped M- α -SiAlON [25]. In 1991, Sun *et al.* [24] supplied two empirical equations based on the pioneering work of Hampshire [26] and abundant experimental data to show this correlation. The equations are listed below:

$$a = 7.752 + 0.045m + 0.009n \quad (1)$$

$$c = 5.620 + 0.048m + 0.009n \quad (2)$$

We also depict these equations with dashed lines in Fig. 2(c) with a series of n values of $n = 0, 1, 2$, and 3 . The data points of parameter c are well below the straight line with $n = 0$, while the data points of parameter a are mostly located between two straight lines with $n = 0$ and $n = 1$. If there is much oxygen in the structure, the lattice parameters should expand and the points of our as-synthesized α -SiAlON should occupy a higher position in Fig. 2(c). Thus, a conclusion can be drawn that little oxygen permeated into the samples during the preparation process. This mild oxygen contamination is probably traceable due to the surface oxidation of Ca_3N_2 powders and the addition of a small quantity of Eu_2O_3 . In addition, SEM observation revealed that the particles of the products have a uniform rod morphology without agglomeration. Fig. 2(d) shows a typical SEM micrograph of the product with $m = 3.18$.

Fig. 3(a) shows the emission spectra of the as-prepared Ca-SiAlON phosphors with varying m values under excitation at 420 nm at room temperature. Meanwhile, the relationship of the integrated intensity of the phosphors and the peak position of the emission spectra with varying m values is depicted in the inset. The emission spectrum showed a single broadband covering a wide range from 520 to 700 nm. This single broadband can be ascribed to the transmission of $5d^14f^6 \rightarrow 4f^7$ from Eu^{2+} , which is greatly affected by the nephelauxetic effect and crystal field splitting of the $5d$ levels. As the m value increased, the photoluminescence intensity of as-prepared SiAlON phosphors significantly increased, and the optimum intensity occurred when $m = 3.18$. This can be well explained by the higher Al^{3+} concentration providing a larger interstitial cavity in the unit cell for the accommodation of cations (i.e., Eu^{2+}). Furthermore, it can be observed from the emission spectra that a notable redshift effect emerged as the m value increased. The previous study of Yang *et al.* suggests that two factors contribute to this redshift phenomenon [25]. First, as the larger Al^{3+} ions occupy the Si^{4+} site, N^{3-} can be slightly displaced and get closer to the luminescence center Eu^{2+} , offering a stronger crystal field. Second, the crystal lattice expands as the m value increases, which results in a decrease in the crystal field strength. Thus, under the combined effect of these two factors, the emission wavelength slightly deviates to a longer band.

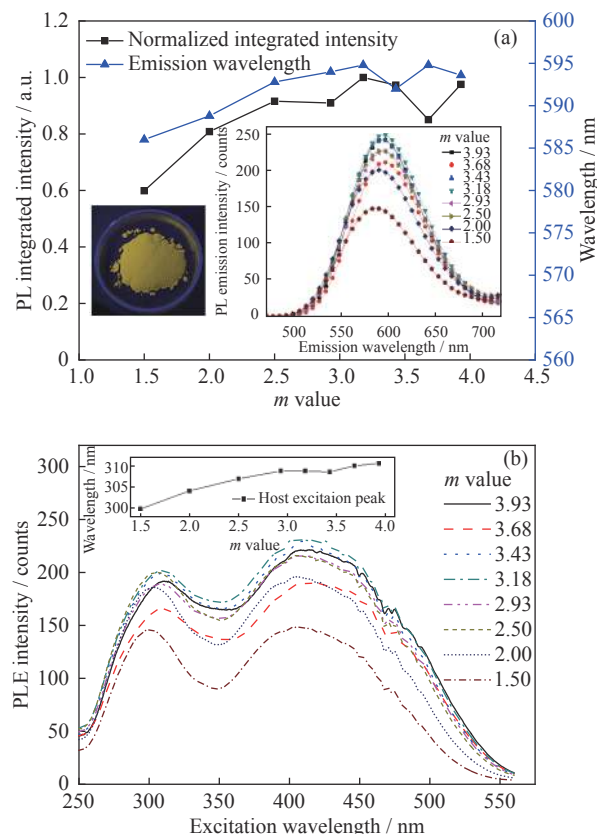


Fig. 3. (a) Photoluminescence (PL) spectra by 420 nm excitation of synthesized Ca-SiAlON:Eu²⁺ phosphors and the photo (Trends of integrated intensity and emission wavelength with m values are plotted in the inset); (b) Photoluminescence excitation (PLE) spectra of as-prepared samples recorded at 600 nm (The relationship of the position of the first peak with m values is plotted in the inset).

Fig. 3(b) shows the excitation spectra of the as-synthesized samples with different m values measured at room temperature and monitored at 600 nm. The excitation spectra are composed of two broad excitation bands, one band centered at approximately 305 nm and the other with a maximum at around 405 nm. The peak near 305 nm is derived from the absorption of the matrix (Ca- α -SiAlON), and the peak near 405 nm is ascribed to the transition of $4f^7 \rightarrow 4f^65d^1$ from Eu^{2+} . The optimum photoluminescence excitation intensity was obtained when m was 3.18, which coincides well with the emission spectra. Additionally, as the m value increases, the first peak shows a tendency to shift to the longer excitation wavelength.

To elucidate the redshift effect, the density of states (DOS) of Ca- α -SiAlON:Eu²⁺ were investigated with first-principle electronic structure calculations. These calculations were performed using the projector augmented wave method [27–28], which was implemented in the Vienna *ab initio* simulation package [29–31]. The generalized gradient approximation of the Perdew–Burke–Ernzerhof [32] type was adopted.

ted to calculate the exchange-correlation energy among interacting electrons. The $4 \times 4 \times 3$ and $8 \times 8 \times 6$ k -point meshes were adopted for the Brillouin-zone sampling in the structural relaxation and the DOS calculations, respectively. The kinetic energy cutoff of the plane-wave basis was set to 400 eV. In structural optimization, the internal atomic sites were allowed to relax until all the forces on atoms were no larger than 0.01 eV/Å. Fig. 4 shows the calculated results for the DOS of Ca- α -SiAlON:Eu²⁺, where three models with $m = 2, 3$, and 4 were performed. With the increase in m value, the conduction band bottom continuously decreases, while the valence band top remains almost unchanged, resulting in a narrowing of the energy gap (Fig. 4(a)). Furthermore, a narrower energy gap corresponds to a longer wavelength of intrinsic absorption, which reasonably agrees with the variation of the excitation spectra (Fig. 3(b)). Further analysis of the local density of states indicates that the valence band top originates from N 2p orbitals (Fig. 4(b)) and the conduction band bottom is mainly contributed by Ca 3d orbitals (Fig. 4(c)); this can be well understood from the sequence of the electronegativity of these atoms: Ca (1.00), Al (1.61), Si (1.90), N (3.04). With a higher Ca content (larger m value), the N 2p orbitals are always fully occupied, and they determine the position of Fermi level; meanwhile, the unoccupied Ca 3d orbitals shift to lower energies and reduce the bandgap.

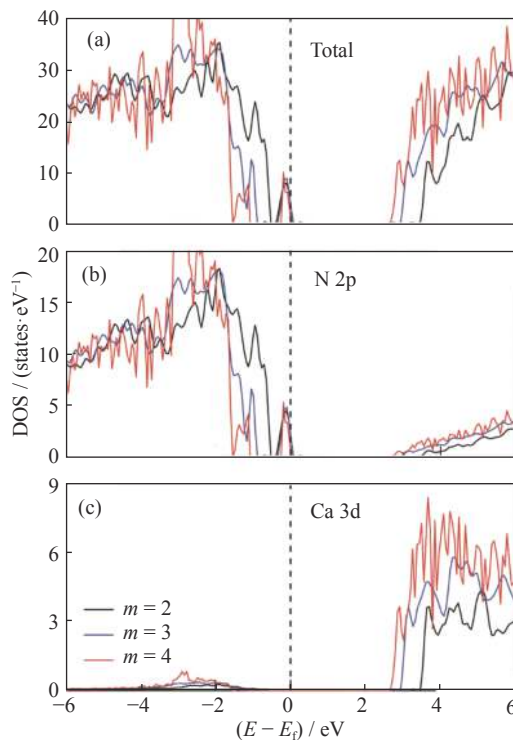


Fig. 4. Total density of states (DOS) (a) and partial DOS for N atoms (b) and Ca atoms (c) in Eu-doped Ca-SiAlON with different m values. In the abscissa, E represents the electron energy and E_f represents the Fermi level.

4. Conclusions

In this work, a freeze-drying assisted combustion synthesis method was adopted for the fabrication of nitrogen-rich Eu²⁺-doped Ca- α -SiAlON phosphors. The findings of this work lead to the following conclusions.

(1) This modified method is relatively simple and fast and yields a product with high purity and uniform morphology.

(2) Low oxygen content in the as-synthesized Ca- α -SiAlON phosphors was confirmed by comparing the Rietveld refinement results with previous empirical equations.

(3) The photoluminescence properties of the products were investigated in detail. The Ca _{$m/2-0.08$} Si _{$12-m$} Al _{m} N₁₆:0.08Eu phosphors showed a broadband emission covering 520–700 nm. When $m = 3.18$, the sample showed optimum luminescence intensity.

(4) Additionally, the electronic structure calculation shows that the valence band top originates from N 2p orbitals and the conduction band bottom is mainly contributed by Ca 3d orbitals. The conduction band bottom continuously decreases as the m value increases, which causes a redshift in the absorption spectrum.

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