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Synthesis and luminescence properties of novel $Y_2Si_4N_6C:Sm^{3+}$ carbonitride phosphor

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Abstract

Novel $Y_2Si_4N_6C:Sm^{3+}$ phosphors for white light-emitting diodes (w-LEDs) were prepared by a carbothermal reduction and nitridation method. X-ray diffraction (XRD) and photoluminescence spectra were utilized to characterize the structure and luminescence properties of the as-synthesized phosphors. The emission spectrum obtained by excitation into 291 nm contains exclusively the characteristic emission of Sm^{3+} at 568, 607 and 654 nm which correspond to the transitions from $^4G_{5/2}$ to $^6H_{5/2}$, $^6H_{7/2}$, and $^6H_{9/2}$ of Sm^{3+}, respectively. The strongest one is located at 607 nm due to $^4G_{5/2}$–$^6H_{7/2}$ transition of Sm^{3+}. It was found that concentration quenching occurred as a result of dipole–dipole interaction according to Dexter's theory. The temperature dependence of photoluminescence properties was investigated from 25 to 300 °C and the prepared $Y_2Si_4N_6C:Sm^{3+}$ phosphors showed superior thermal quenching properties.

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Keywords: Luminescence; Red phosphors; W-LEDs; Optical materials

1. Introduction

In recent years, oxynitride and nitride compounds have attracted much attention as host lattices for phosphors because of their excellent properties, such as non-toxicity, outstanding thermal and chemical stability, broad available range of excitation and emission wavelengths, and high luminescence efficiency [1,2,3]. This feature allows nitrides and oxynitrides to be good candidates as the phosphors for white light emitting diodes (w-LEDs). The white LEDs can be fabricated by using a blue InGaN LED chip in combination with a yellow phosphor of cerium (III)-doped yttrium aluminum garnet (YAG:Ce^{3+}) [4]. The white LED based on YAG:Ce^{3+} phosphor suffers from strong thermal quenching and exhibits a poor color rendering index (CRI ≈ 70–80) and a high correlated color temperature (CCT ≈ 7750 K) because of lacking a red component [5]. Consequently, an additional phosphor to compensate the red deficiency of YAG:Ce^{3+}-based LED is necessary. Among all candidates for the red phosphors, the tetrahedral SiN_4-based nitrides show much promising potential compared with the conventional alkaline earth silicate or sulfide phosphors due to their high mechanical hardness and their exceptional thermal and chemical stability [6]. Representative candidates are $M_2Si_5N_8:Eu^{2+}$ (M = Ca, Sr, Ba) $CaAlSiN_3:Eu^{2+}$. Both have an unusual longer-wavelength emission of Eu^{2+} and wider absorption bands in the UV-visible range. In particular, $CaAlSiN_3:Eu^{2+}$ with an orthorhombic crystal structure and the space group of $Cmc2_1$, which has many advantages, including high resistance to most chemicals, temperature quenching, and mechanical strength attributable to its rigid crystal structure, seems most promising for applications in which saturated red is required [7]. Recently, yttrium silicon carbonitride, $Y_2Si_4N_6C$, has been reported as a new compound. Structurally, they are derived from the quaternary silicon nitride compounds, $MRESi_4N_7$ (M = Ca, Sr, Ba; RE = Y, Yb), by formal substitutions of nitrogen by carbon and M^{2+} by RE^{3+}. The high structural stability of the carbonitride phosphors is expected due to the strong covalency of N^{3-} and C^{4-} in the host lattice [8].

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In this paper, we report the luminescence properties and decay times of $Y_2Si_4N_6C:Sm^{3+}$ phosphor. The concentration quenching and thermal quenching properties of Sm^{3+} in $Y_2Si_4N_6C$ were investigated. This could be helpful in understanding the quenching mechanisms and developing new materials that have potential application for W-LEDs.

2. Experimental

2.1. Sample preparation

The red-emitting phosphors of $Y_{2-x}Si_4N_6C:xSm^{3+}$ ($x=0.004$, 0.008, 0.012, 0.015, and 0.03) were synthesized via a carbothermal reduction nitridation (CRN) route. The starting material was a stoichiometric mixture of reagent grade Y_2O_3 (99.9%), Si_3N_4 (99.9%), Sm_2O_3 (99.9%), C (graphite, 99^+%). Firstly, the powder mixtures were transferred into a closed molybdenum crucible and were fired at 1650 °C for 10 h in a chamber furnace under a nitrogen atmosphere. After that, the resulting samples were fired again in air at 600 °C for 20 h to remove the residual carbon. However, the X-ray diffraction (XRD) pattern of samples had no obvious change after such firing.

2.2. Sample characterization

The crystal structure of the as-synthesized samples were identified by using powder X-ray diffraction analysis with a Shimadzu model XRD-6000 X-ray powder diffraction with Cu $K\alpha$ radiation, 40 kV, 30-mA, and a scan speed of $2.0°(2\theta)$/min. The VIS emission spectrum was recorded by using a Hitachi F-7000 fluorescence spectrophotometer and a 150 W Xe lamp was used as the excitation lamp. Luminescent decay curves were measured by using a FluoroLog-3 spectrofluorometer (HORIBA JBOINY-VON, USA) with Spectra LED (S-370) as the excitation source and a R928P photomultiplier for signal detection. Additionally, thermal quenching and activation energy were detected with the heating apparatus (TAP-02).

3. Results and discussions

3.1. Crystal structure

Fig. 1 shows the X-ray diffraction (XRD) patterns of as-prepared $Y_2Si_4N_6C:Sm^{3+}$. The XRD patterns of the sample are consistent with Powder Diffraction Standards (ICSD) card no. 155158, indicating that doping of a small content of Sm^{3+} ion did not change the lattice structure. $Y_2Si_4N_6C:Sm^{3+}$has a monoclinic crystal structure and the space group of $P2_1/c$ with unit cell volume and lattice parameters are 605.92 Å^3, $a=5.9295$ Å, $b=9.8957$ Å, $c=11.8800$ Å, and $\beta=119.63°$ [9]. In compound $Y_2Si_4N_6C$, there are two types of Y^{3+} atoms. As shown in Fig. 2, The Y1 site is coordinated by five N atoms. Each N atom connects with two Si atoms and coordinates two neighboring Y atoms at the same time. The Y2 site is coordinated by six N atoms. Each N atom connects with two Si atoms, but only five of these six N atoms coordinate two Y atoms and N coordinates only one Y atom [10].

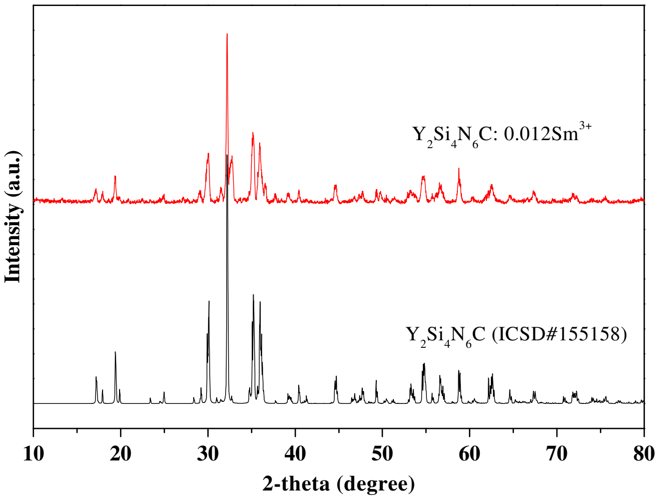

Fig. 1. XRD patterns of $Y_2Si_4N_6C:0.012Sm^{3+}$, and the standard data $Y_2Si_4N_6C$ (ICSD No. 155158) as a reference.

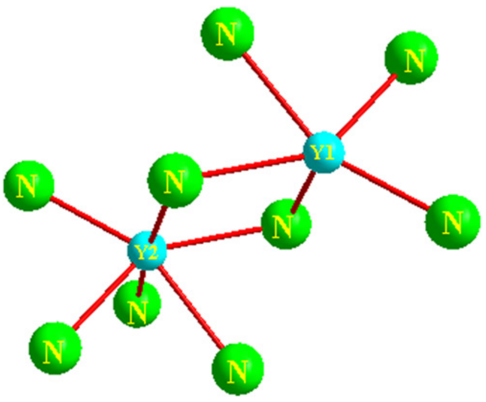

Fig. 2. Nitrogen atom coordination of the two different Y^{3+} sites in $Y_2Si_4N_6C$.

3.2. Luminescence properties of $Y_2Si_4N_6C:Sm^{3+}$

The Sm^{3+} ion with $4f^5$configuration has complicated energy levels and different conceivable transitions inter f levels. Under the excitation of short ultraviolet, the $Y_2Si_4N_6C:Sm^{3+}$ exhibits a red luminescence. Fig. 3(a) describes the PLE spectra of the $Y_2Si_4N_6C:0.012Sm^{3+}$ sample. It can be seen that the excitation spectrum of $Y_2Si_4N_6C:0.012Sm^{3+}$ consists of a broad excitation band in the range of 200–350 nm due to the $Sm^{3+} \rightarrow N^{3-}$ charge transfer transition and some weak lines at 363, 378 and 410 nm which can be assigned to the transitions from the ground $^6H_{5/2}$ level to $^4D_{15/2}$ (363 nm), $^6H_{5/2}$ (378 nm) and $^4K_{11/2}$ (410 nm), respectively [11,12]. The emission spectrum (Fig.3(b)) obtained by excitation into 291 nm contains exclusively the characteristic emission of Sm^{3+} at 568, 607 and 654 nm which correspond to the transitions

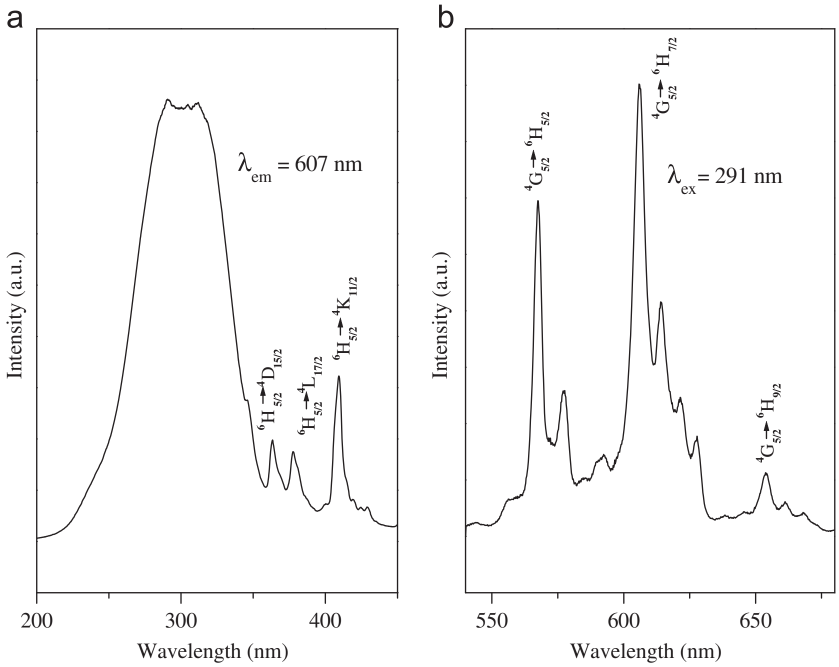

Fig. 3. Photoluminescence excitation (a) and emission (b) spectra of $Y_2Si_4N_6C$:$0.012Sm^{3+}$.

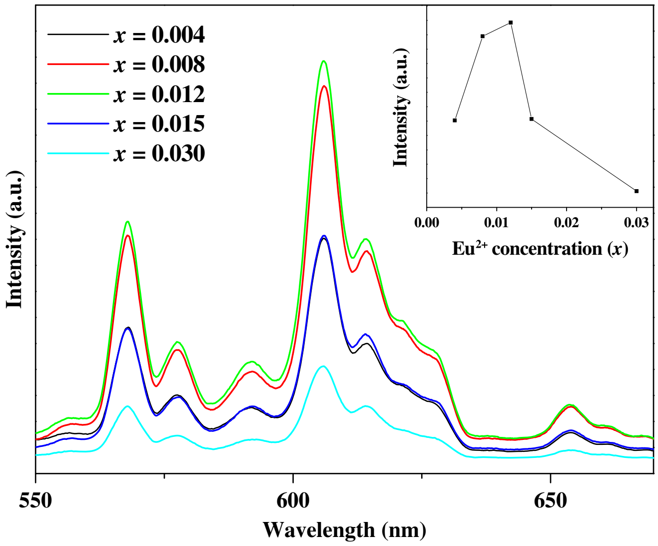

Fig. 4. PL spectra of $Y_2Si_4N_6C$:$0.012Sm^{3+}$ phosphors (λ_{ex}=291 nm) for various concentrations: x=0.004, 0.008, 0.012, 0.015, 0.030, respectively. The inset shows Sm^{3+} concentration of relative luminescence intensity at 607 nm.

from $^4G_{5/2}$ to $^6H_{5/2}$, $^6H_{7/2}$, and $^6H_{9/2}$ of Sm^{3+}, respectively. The strongest one is located at 606 nm due to $^4G_{5/2}$–$^6H_{7/2}$ transition of Sm^{3+}. The excitation and emission spectra indicate that $Y_2Si_4N_6C$:Sm^{3+} phosphor is a promising red phosphor for W-LEDs.

3.3. Concentration quenching of $Y_2Si_4N_6C$:Sm^{3+}

Fig. 4 shows the dependence of the relative emission intensities of the $Y_{2-x}Si_4N_6C$:xSm^{3+} (x=0.004, 0.008, 0.012, 0.015, and 0.03) phosphors on the Sm^{3+} doping concentrations. As the Sm^{3+} concentration increases, the emission intensity increases and it achieves a maximum at x=0.012. The concentration quenching occurs when x is beyond 0.012. The inset displays the variation of the intensity as a function of Sm^{3+} concentration.

The energy transfer from one activator to another generated the concentration quenching of the luminescence. With respect to the mechanism of energy transfer in phosphors, Blasse has pointed out that the critical transfer distance (Rc) is approximately equal to twice the radius of a sphere with the equation [13]:

$$R_C = 2\left[\frac{3V}{4\pi x_c N}\right]^{1/3} \tag{1}$$

where the V is the volume of the unit cell, x_c is the critical concentration of activator ion, and N is the number of cations in the unit cell. For $Y_2Si_4N_6C$ host V=605.92 Å^3, N=4, x_c=0.012, the obtained R_c value of Sm^{3+} was found to be 28.89 Å.

Generally, there are main two aspects responsible for the resonant energy-transfer mechanism: one is exchange interaction and the other is multipolar interaction. It is known that if energy transfer results from the exchange interaction, the critical distance between the sensitizer and activator should be shorter than 3–4 Å [14], which is far less than that of the sated calculation result of Sm^{3+}-doped in $Y_2Si_4N_6C$. This suggests that the energy transfer between Sm^{3+} ions in $Y_2Si_4N_6C$:Sm^{3+} phosphor does not occurred in this case. According to Dexter's theory [15], if the energy transfer occurs between the same sorts of activators, the strength of the multipolar interaction can be determined from the change in the emission intensity from the emitting level which has the multipolar interaction. The emission intensity (I) per activator ion follows the equation [16,17].

$$\frac{1}{x} = K[1+\beta(x)^{Q/3}]^{-1} \tag{2}$$

Here x is the activator concentration; $Q=6$, 8 or 10 for dipole–dipole, dipole–quadrupole or quadrupole–quadrupole interaction, respectively; and K and β are constants for the same excitation condition for a given host crystal. It can be seen from Fig. 5 that the dependence of $\log[\mathrm{I}/x_{\mathrm{Sm}}^{3+}]$ on $\log(x_{\mathrm{Sm}}^{3+})$ is linear and the slope is -2.049. The value of Q can be calculated as 6.147, which is approximately equal to 6, by using Eq. (2). This indicates that the dipole–dipole interaction is the major mechanism for concentration quenching of the central Sm^{3+} emission in $Y_2Si_4N_6C:Sm^{3+}$ phosphor.

Based on the above-mentioned emission spectra of samples, the relationship between concentration quenching behavior and decay time is considered. Fig. 6 shows the decay curves of the Sm^{3+} in $Y_{2-x}Si_4N_6C:xSm^{3+}$ ($x=0.004$, 0.008, 0.012, 0.015, and 0.03). The corresponding luminescence decay times can be calculated by double-exponential decay mode according to the following equation [18]:

$$I = \mathrm{A_1exp}(-\mathrm{t}/\tau_1)+\mathrm{A_2exp}(-\mathrm{t}/\tau_2) \tag{3}$$

where I is the luminescence intensity; A_1 and A_2 are constants; t is the time, and τ_1 and τ_2 are decay time for exponential. According to these parameters, the average decay times (τ) of Sm^{3+} can be calculated by the following equation:

$$\tau = \frac{A1\tau_1^2+A2\tau_2^2}{A1\tau_1+A2\tau_2} \tag{4}$$

The effective lifetime values were calculated to be 0.5197, 0.4673, 0.4013, 0.3129, and 0.1896 ms for $Y_{2-x}Si_4N_6C:x$ Sm^{3+} phosphors with $x=0.004$, 0.008, 0.012, 0.015, and 0.03 respectively. The inset in Fig. 6 depicts the decay time of several Sm^{3+} concentration under 410 nm excitation. It obviously shows that the decay time begins to decrease suddenly at around 0.012 and the luminance, which was defined as the area under the corresponding peaking, displays the similar behavior. Actually, the nonradiative and self-absorption rate of the internal doped ions evidently increase when activators cross the critical separation between donor (activator ion) and acceptor (quenching site) [19].

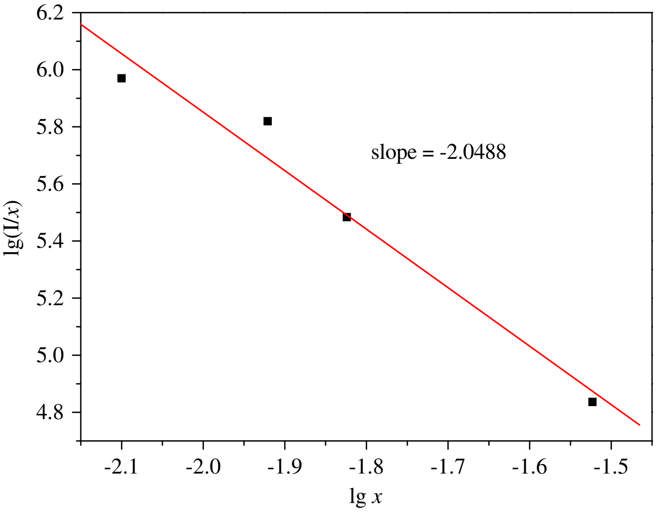

Fig. 5. Curve of log (I/x) vs. log x in $Y_2Si_4N_6C:0.012Sm^{3+}$ phosphor for the emission band peaking around 607 nm.

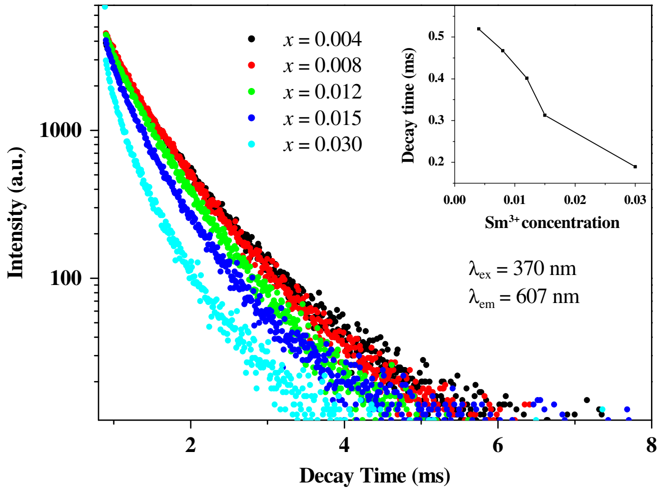

Fig. 6. Decay curves of Ce^{3+} emission of $Y_2Si_4N_6C:xSm^{3+}$ ($x=0.004$, 0.008, 0.012, 0.015, 0.030) excited at 370 nm and monitored at 607 nm.

3.4. Thermal quenching of $Y_2Si_4N_6C:Sm^{3+}$

In general, the temperature dependence of W-LEDs phosphors is important because it has great influence on the light output and color rendering index [20,21]. Phosphors must sustain emission efficiency at temperatures about 150 °C over a long-term when they are used in W-LEDs. It is thus required that the thermal quenching of phosphors should be small, typically for high-power ones [22]. Fig. 7 shows typical PL spectra of the $Y_2Si_4N_6C:Sm^{3+}$ phosphors measured in a temperature range from 25 to 300 °C. An unexpected phenomenon has been observed that the emission intensity at 607nm originated from $^4G_{5/2}\rightarrow{}^6H_{7/2}$ transition increases slowly on heating from 25 to 200 °C, and then decreases dramatically for temperatures above 200 °C under the excitation at 410 nm, which indicates $Y_2Si_4N_6C:Sm^{3+}$ phosphor has comparatively low temperature quenching effect. The inset shows that the thermal stability of $Y_2Si_4N_6C:Sm^{3+}$ is higher than that of the commercially available YAG:Ce phosphor and other rare-earth doped phosphate phosphors [23,24]. One can see that, for all compositions no shift in the emission band is observed when the temperature raises, indicative of stable chromaticity coordinates of $Y_2Si_4N_6C:Sm^{3+}$ phosphors. It is believed that no shift in color point is due to the rigid crystal structure of the $Y_2Si_4N_6C$ host lattice built up on $[C(SiN_3)_4]$ tetrahedral networks. All the phenomena

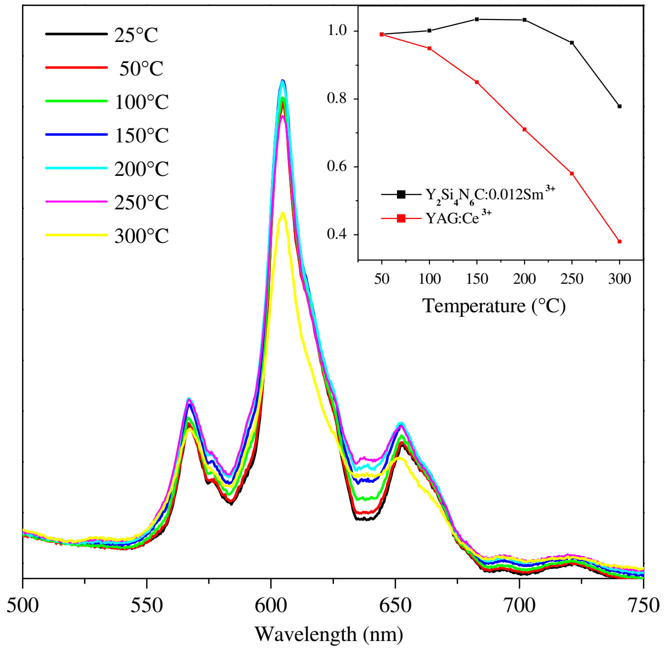

Fig. 7. PL spectra of $Y_2Si_4N_6C$:0.012Sm^{3+} for various temperatures; the insets show the corresponding integrated emission intensity at different temperatures.

may be due to the good thermal stability and chemical stability of $Y_2Si_4N_6C$:Sm^{3+} phosphor, which will be crucial for its potential application in WLEDs.

4. Conclusions

In summary, A novel $Y_2Si_4N_6C$:Sm^{3+} phosphors were synthesized by a carbothermal reduction and nitridation method and its luminescent properties are investigated. The phosphor has three emission bands centering at 568, 607 and 654 nm which correspond to the transitions from $^4G_{5/2}$ to $^6H_{5/2}$, $^6H_{7/2}$, and $^6H_{9/2}$ of Sm^{3+}, respectively. The phosphor shows broad excitation band from 250 to 420 nm, which can be effectively excited by UV chips (360–400 nm) for the potential applications in the W-LEDs. According to the experimental results and the theoretical calculation, it is identified that the dipole–dipole interaction plays the major role in the concentration quenching mechanism of Sm^{3+} in $Y_2Si_4N_6C$:Sm^{3+} phosphor. The temperature-dependent PL spectra show that the obtained phosphors have the good thermal stability for its potential application.

Acknowledgments

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