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# High temperature stability of $Eu^{2+}$-activated nitride red phosphors

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**Abstract:** The novel nitride-based luminescent materials have received much attention since the end of the last century. In this paper, the commercial $Eu^{2+}$-activated nitride red phosphors, $Sr_{1.95}Si_5N_8:Eu_{0.05}$, $Sr_{1.85}Si_5N_8:Eu_{0.15}$ and $Ca_{0.99}AlSiN_3:Eu_{0.01}$ phosphors were annealed at different temperatures (beyond 300 ºC) to investigate the dependence of their luminescence performance and structure variability on the temperature. By photoluminescence spectra, X-ray diffraction (XRD) and thermogravimetry-differential scanning calorimetry (TG-DSC) analysis, the high temperature stability of the hosts and activator of the three samples were disclosed. With the annealing temperature increasing, the activator $Eu^{2+}$ ions were firstly oxidized and then host in $Sr_{1.95}Si_5N_8:Eu_{0.05}$ and $Sr_{1.85}Si_5N_8:Eu_{0.15}$, but for $Ca_{0.99}AlSiN_3:Eu_{0.01}$, only the oxidation of the host could be observed, which would lead to the luminescence degradation and even failure of these phosphors. The activator $Eu^{2+}$ ions were much more stable in $CaAlSiN_3:Eu$ than $Sr_2Si_5N_8:Eu$ due to their crystal surroundings, and its concentration also influenced the temperature stability of $Sr_2Si_5N_8:Eu$.

**Keywords:** nitride; red phosphor; high temperature stability; oxidation; rare earths

Since the end of the last century, rare earth-activated (oxy)nitride phosphors, a new family of luminescent materials, have attracted much attention because of their desirable properties for GaN-based white LEDs (light emitting diodes) application. Compared with the traditional oxide-, sulfide- and oxysulfide-based phosphors, (oxy)nitride phosphors usually have superior thermal and chemical stability. In particular, the red-light emitting nitride phosphors, $M_2Si_5N_8:Eu$ and $MAlSiN_3:Eu$ (M: alkali earth metal), have high light-converting efficiency and excellent stability, and are widely substituting for unstable sulfide phosphors as commercial red phosphors to compensate white LEDs for red deficiency and produce highly efficient and reliable white LEDs with higher color rendering index (CRI) and lower color temperature ($T_c$)[1–5].

Extensive investigations and efforts have been made to prepare and study the photoluminescence of both nitride red phosphors[4–23]. For instance, as one of the important application performance, the temperature characteristics (≤300 ºC) of these nitride red phosphors were focused on by many reports[6–13]. According to these research results, the luminescent intensities of $M_2Si_5N_8:Eu$ and $MAlSiN_3:Eu$ at 150 ºC can remain about 86% and 89% of that at room temperature, respectively, which is superior to that of the conventional sulfide red phosphor.

In order to investigate the physical and chemical properties of nitride phosphors in details, in present work, we selected $Sr_{1.95}Si_5N_8:Eu_{0.05}$, $Sr_{1.85}Si_5N_8:Eu_{0.15}$ and $Ca_{0.99}AlSiN_3:Eu_{0.01}$ phosphors to study their luminescent performance and structure variability before and after being annealed at different temperatures (beyond 300 ºC). The influence of activator Eu concentration was considered. Firstly, the desired Eu concentration 0.05 and 0.01 for $Sr_2Si_5N_8:Eu$ and $CaAlSiN_3:Eu$ was selected; at the same time, Eu0.15 in $Sr_2Si_5N_8:Eu$ was also involved in the present work. By photoluminescence spectra, XRD and TG-DSC analysis, the high temperature stability of the hosts and activator $Eu^{2+}$ ions of the three samples were disclosed.

## 1 Experimental

$Sr_{1.95}Si_5N_8:Eu_{0.05}$, $Sr_{1.85}Si_5N_8:Eu_{0.15}$ and $Ca_{0.99}AlSiN_3:Eu_{0.01}$ phosphor samples were firstly prepared by the high temperature solid state reaction method under normal pressure as described earlier[9–11], and then were annealed at 200, 300, 400, 500, 700 and 1000 ºC for 30 min in air, respectively. The thermal stability of these phosphors at the high temperature can be detected by comparing the structure and photoluminescence performance of the samples before and after annealing.

Thermogravimetric and calorimetric analyses of the

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phosphor samples were recorded on a Netzsch STA 449C simultaneous TG-DSC instrument at a heating rate of 10 ºC/min. XRD identification was checked by a Bruker D8 Advance X-ray powder diffractometer running Cu Kα radiation at 40 kV and 40 mA, and the XRD patterns were collected in the range of 15º≤2*θ*≤65º. The emission spectra were performed by using an Edinburgh FLS920P fluorescence spectrometer equipped with a 450 W xenon lamp as an excitation source.

## 2 Results and discussion

### 2.1 Luminescence of the annealed nitride phosphors

Figs. 1(a), (b) and (c) present the normalized emission spectra of the unannealed $Sr_{1.95}Si_5N_8:Eu_{0.05}$, $Sr_{1.85}Si_5N_8:Eu_{0.15}$ and $Ca_{0.99}AlSiN_3:Eu_{0.01}$ phosphors and their annealed samples excited by 460 nm blue light, respectively; wherein the annealing temperatures, 200, 300, 400, 500, 700 and 1000 ºC were considered.

As shown in Figs. 1(a), (b) and (c), the emission peaks of the unannealed $Sr_{1.95}Si_5N_8:Eu_{0.05}$, $Sr_{1.85}Si_5N_8:Eu_{0.15}$ and $Ca_{0.99}AlSiN_3:Eu_{0.01}$ phosphors are located at 618, 642 and 660 nm, respectively. With the annealing temperature increasing, the red emission peaks of the annealed samples are slightly moved to short wavelength, and the emission intensity gradually becomes weaker and weaker. For instance, after the three samples were annealed at 500 ºC for 30 min, their emission peaks are blueshifted to 614, 633 and 652 nm, and the relative intensities are degraded to about 58%, 8% and 97% of the corresponding unannealed samples, respectively. Especially, after being annealed at 700 ºC, the obtained $Sr_{1.95}Si_5N_8:Eu_{0.05}$ and $Sr_{1.85}Si_5N_8:Eu_{0.15}$ samples exhibit no photoluminescence phenomena, and $Ca_{0.99}AlSiN_3:Eu_{0.01}$ sample holds only about 18% peak intensity of the unannealed sample. While the annealing temperature reached 1000 ºC, in all three annealed samples no photoluminescence signals can be detected, and they quench completely.

Although $Sr_{1.95}Si_5N_8:Eu_{0.05}$ and $Sr_{1.85}Si_5N_8:Eu_{0.15}$ phosphors belong to the same $Sr_2Si_5N_8:Eu$ category, and their luminescence failure emerges from annealing temperature 700 ºC, it can also be noticed that, with the annealing temperature increasing, the luminescent intensity of $Sr_{1.85}Si_5N_8:Eu_{0.15}$ with higher activator Eu concentration drops more sharply than that of $Sr_{1.95}Si_5N_8:Eu_{0.05}$ with lower Eu concentration. It implies that the $Sr_2Si_5N_8:Eu$ phosphor is very sensitive to the annealing temperature; and furthermore, the higher activator concentration is, the more sensitive the luminescence of the phosphor is to the annealing temperature.

As for another category of nitride phosphors, $Ca_{0.99}AlSiN_3:Eu_{0.01}$ exhibits better stability under high temperature annealing treatment. As shown in Fig. 1(c), when the phosphor sample was annealed below 500 ºC, its emission intensity declines slightly (approximately 3%). And its luminescence failure occurs at annealing temperature 1000 ºC.

### 2.2 XRD analysis

Based on the above analyses, $Sr_{1.95}Si_5N_8:Eu_{0.05}$ and $Sr_{1.85}Si_5N_8:Eu_{0.15}$ phosphors degrade worse when the annealing temperature is beyond 500 ºC, while that of $Ca_{0.99}AlSiN_3:Eu_{0.01}$ beyond 700 ºC. In order to disclose the high temperature failure mechanism of these nitride red phosphors, we compared the XRD patterns of $Sr_{1.95}Si_5N_8:Eu_{0.05}$, $Sr_{1.85}Si_5N_8:Eu_{0.15}$ and $Ca_{1.99}AlSiN_3:Eu_{0.01}$ phosphors and their annealed samples at 500, 700 and 1000 ºC, as shown in Figs. 2(a), (b) and (c), respectively. For unannealed $Sr_{1.95}Si_5N_8:Eu_{0.05}$ and $Sr_{1.85}Si_5N_8:Eu_{0.15}$ phosphor samples, their XRD patterns agree well with JCPDS No. 85-0101, i.e. $Sr_2Si_5N_8$, showing the orthorhombic crystal structure of single $Sr_2Si_5N_8:Eu$ powder prepared in this research. The XRD pattern of the unannealed $Ca_{0.99}AlSiN_3:Eu_{0.01}$ phosphor is similar to that reported by Piao et al.[13], indicating that this phosphor is pure $CaAlSiN_3$ phase with orthorhombic crystal structure.

As depicted in Fig. 2(a) and (b), $Sr_2Si_5N_8:Eu$ category phosphors, $Sr_{1.95}Si_5N_8:Eu_{0.05}$ and $Sr_{1.85}Si_5N_8:Eu_{0.15}$ go through the same phase evolution with elevation at the annealing temperature. After being annealed at 500 ºC, both samples show the similar XRD patterns with their unannealed ones, except for descent in intensities of the diffraction peaks. New diffraction peaks at 2*θ* about 25° are clearly detected and distinguished in the XRD patterns of 700 ºC annealed $Sr_{1.95}Si_5N_8:Eu_{0.05}$ and

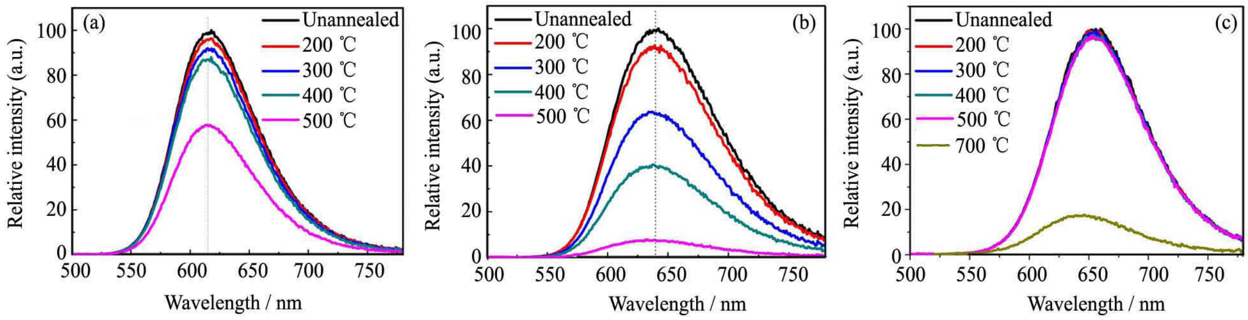


Fig. 1 Emission spectra of the three nitride red phosphors annealed at different temperatures
(a) $Sr_{1.95}Si_5N_8:Eu_{0.05}$; (b) $Sr_{1.85}Si_5N_8:Eu_{0.15}$; (c) $Ca_{1.99}AlSiN_3:Eu_{0.01}$