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Photoluminescence and thermal stability of yellow-emitting Sr-α-SiAlON:Eu^{2+} phosphor

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Abstract Novel α-SiAlON:Eu^{2+}-based yellow oxynitride phosphors with the formula $Sr_{0.375-x}Eu_x^{2+}Si_{12-m-n}Al_{m+n}O_nN_{16-n}$ ($m = 0.75$, $n = x = 0.004$–0.04) have been prepared by firing the powder mixture of $SrSi_2$, α-Si_3N_4, AlN, and Eu_2O_3 at 2,000 °C for 2 h under 1 MPa nitrogen atmosphere. The luminescence properties, the dependence of the activator concentration of Eu^{2+} and the thermal stability of Sr-α-SiAlON:Eu^{2+} phosphor have been investigated in comparison with Ca-α-SiAlON:Eu^{2+} phosphor. Similar to Ca-α-SiAlON:Eu^{2+} phosphor, Sr-α-SiAlON:Eu^{2+} phosphor has the excitation wavelength ranging from the ultraviolet region to 500 nm, and exhibit intense yellow light. The strongest luminescence was achieved at about $x = 0.02$ with the emission peak at 578 nm, slightly shorter than that of Ca-α-SiAlON:Eu^{2+} phosphor at 581 nm. Temperature-dependent emission intensity of Sr-α-SiAlON:Eu^{2+} phosphor is comparable to that of Ca-α-SiAlON:Eu^{2+} phosphor. The results suggest that the different position of the emission peak for Sr- and Ca-α-SiAlON:Eu^{2+} depends on the composition and the Stokes shift, and the thermal stability is nearly independent of Sr and Ca or fixed by the network of (Si, Al)–(O, N) in α-SiAlON at the same Eu^{2+} concentration.

Introduction

Solid-state lighting, which uses white light-emitting diodes (white-LEDs) is considered as next generation lighting systems because it has potential to significantly surpass the power consumption of traditional incandescent and fluorescent lighting, and promises compactness, long lifetime, and environmental friendliness (due to without toxic mercury). The first commercially available white-LED was prepared by pumping the most commonly used yellow phosphor [Ce^{3+}—activated yttrium aluminum garnet (YAG:Ce^{3+})] with a blue LED [1]. In this device, the blue LED light combines with the yellow light that comes from the phosphor to generate whitish light. However, it is impossible to generate “warm” white light using the YAG:Ce^{3+} phosphor only because of their less red luminescence. Furthermore, the phosphor is desired to exhibit high thermal stability when combined with recent high-power blue-LED chips. This is because that high junction temperature of the high-power LED chip will lead to much amount of heat to cause the thermal degradation of phosphors and reduce the luminescent properties such as chromaticity stability and brightness. Therefore, it is necessary to explore yellow-emitting luminescent materials that exhibit simultaneous wavelength and high thermal stability in both brightness and chromaticity.

Rare-earth-doped oxynitride or nitride luminescent materials have become the most important wavelength-conversion phosphors for use in white-LEDs embedded on (In, Ga)N chips due to their strong absorption and high conversion efficiency in UV-blue and blue spectral range. Typical examples are red-emitting $M_2Si_5N_8$:Eu^{2+} (M = Ca, Sr, and Ba) [2, 3] and $CaAlSiN_3$:Eu^{2+} [4, 5], yellow-emitting Ca-α-SiAlON:Eu^{2+} [6–9], green-emitting β-SiAlON:Eu^{2+} [10], and yellow-emitting Ce-melilite

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[11]. Among these (oxy)nitride luminescence materials, Ca-α-SiAlON:Eu^{2+} phosphor has strong absorption in the range of UV to blue region and exhibits a broad yellow emission band ranging from 550 to 590 nm [7]. It has been demonstrated that the Ca-α-SiAlON:Eu^{2+} phosphor is a good yellow phosphor for creating white light when combined with a blue or UV-LED chip [12]. In addition, the α-SiAlON host lattice is very flexible for material design without changing the crystal structure, and degrading the chemical and thermal stability, as its basic structure is based on (Si, Al)–$(O, N)_4$ tetrahedral networks.

α-SiAlON has an overall composition given by the formula:

$$M_{m/v}Si_{12-m-n}Al_{m+n}O_nN_{16-n}, \tag{1}$$

where M is the modifying cations such as Li, Mg, Ca, Y, and rare earth (excluding La, Ce, Pr, and Eu), and v is the valence of the cation M. The crystal structure of α-SiAlON is derived from α-Si_3N_4 by partial replacement of Si^{4+} by Al^{3+} and N^{3-} by O^{2-} simultaneously, as well as stabilized by trapping cations M into the interstices of the (Si, Al)–$(O, N)_4$ network [13]. It was generally accepted that Sr^{2+} ion alone cannot stabilize the α-SiAlON structure due to its large ionic size, but it can if co-doped with calcium or yttrium [14]. Recently, the synthesis, crystal structure, and photoluminescence on Sr containing α-SiAlON ($Sr_{m/2}Si_{12-m-n}Al_{m+n}O_nN_{16-n}$:$Eu^{2+}$) phosphor with compositions having small m and n values has been reported [15]. Our previous study of Sr containing α-SiAlON phosphor mainly focused on the synthesis and crystal structure, therefore, in this article as a subsequent work we investigated the photoluminescence spectrum, concentration quenching, and thermal stability of Sr-α-SiAlON:Eu^{2+}, and compared these with Ca-α-SiAlON:Eu^{2+}. At last, we attempted to apply Sr-α-SiAlON:Eu^{2+} in white-LEDs by integrating with an InGaN-based blue-LED chip (445 nm), and reported the optical properties of white-LEDs.

Experimental

Sr-α-SiAlON:Eu^{2+} samples were prepared from α-Si_3N_4 (SN-E10, Ube Industries Ltd., Japan), $SrSi_2$ (Kojyundo Chemical Laboratory Co. Ltd., Japan), AlN (Type F, Tokuyama Co. Ltd., Japan), and Eu_2O_3 (Shin-Etsu Chemical Co. Ltd., Japan). $SrSi_2$ was used as the Sr^{2+} source to prepare the compositions with small n, because it is very stable against oxygen compared with metal Sr or metal nitride Sr_3N_2. The powder mixtures with nominal compositions $Sr_{0.375-x}Eu_xSi_{11.25}Al_{0.75}O_nN_{16-n}$ ($m = 0.75$, $n = x = 0.004$–0.04) were ground in the Si_3N_4 mortar and pestle. As reported previously [15], Sr containing α-SiAlON was obtained as a major phase in compositions having small m and n values, and the concentration of dopant (x) was varied in a range of $x = 0.004$–0.04. The mixed powders were bedded in h-BN crucibles and then fired in a graphite resistance furnace at 2,000 °C for 2 h under 1 MPa nitrogen atmosphere. The Eu^{3+} ion introduced in the form of Eu_2O_3 was reduced to Eu^{2+} under the nitrogen/CO atmosphere during firing, which is confirmed by the absorption and emission spectra given later. For comparison, Ca-α-SiAlON samples with nominal compositions $Ca_{0.375-x}Eu_xSi_{11.25}Al_{0.75}O_xN_{16-x}$ ($m = 0.75$, $n = x = 0.004$–0.04) were also prepared by using the same firing conditions.

The X-ray diffraction (XRD) patterns of the obtained products were recorded at 40 kV and 40 mA using Cu Kα radiation (Ultima III, Rigaku, Japan). A step size of 0.02° 2θ was used with a scanning speed of 2°/min. The local structure around Sr (Eu^{2+}) or Ca (Eu^{2+}) ions was visualized using the software package VESTA [16]. The photoluminescence spectra of the powder samples were measured by a fluorescent spectrophotometer (Model F-4500, Hitachi Ltd., Japan) at room temperature with a 150 W Ushio xenon short arc lamp. The emission spectrum was corrected for the spectral response of a monochrometer and Hamamatsu R928P photomultiplier tube by a light diffuser and tungsten lamp (Noma, 10 V, 4 A). The excitation spectrum was also corrected for the spectral distribution of the xenon lamp intensity by measuring rhodamine-B as the reference. Temperature-dependent luminescence properties were recorded on an intensified multichannel spectrophotometer (Otsuka Electrics, MCPD-7000) with a 200 W Xe-lamp as an excitation source. The powder samples were heated from room temperature to 300 °C with a heating rate of 100 °C/min, and kept for 5 min for each temperature point. The single phosphor LED was fabricated by coating Sr-α-SiAlON:Eu^{2+} yellow phosphor in silicone on an InGaN blue-LED chip (445 nm) as the primary light source. The optical properties were measured by MCPD-7000 under a forward-bias current 20 mA at room temperature.

Results and discussion

Dependence of photoluminescence properties of Sr-α-SiAlON:Eu^{2+} on the host lattice

Figure 1 shows the XRD patterns of (a) Sr-α-SiAlON:Eu^{2+} and (b) Ca-α-SiAlON:Eu^{2+} with the nominal compositions $Sr_{0.355}Eu_{0.02}Si_{11.23}Al_{0.77}O_{0.02}N_{15.98}$ and $Ca_{0.355}Eu_{0.02}Si_{11.23}Al_{0.77}O_{0.02}N_{15.98}$ ($x = 0.02$). As seen in Fig. 1, the α-SiAlON phase was obtained as a major phase and $SrSi_6N_8$ as a minor phase, indicating that Sr^{2+} can also stabilizes the α-SiAlON structure. Figure 2 shows the

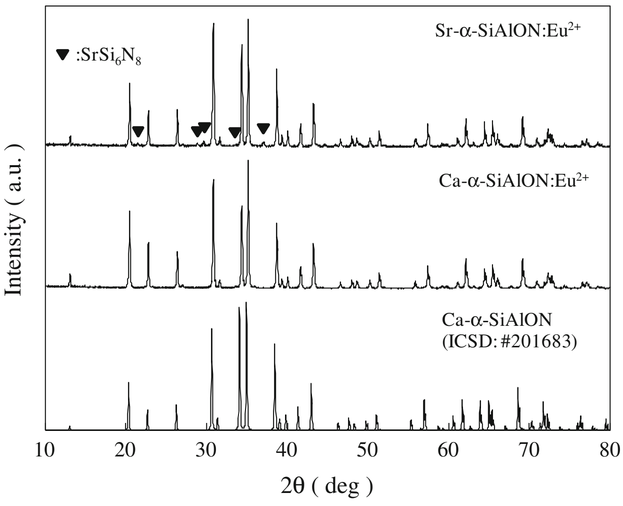

Fig. 1 X-ray powder diffraction patterns of Sr-α-SiAlON:Eu^{2+}, Ca-α-SiAlON:Eu^{2+}, and simulated XRD pattern (Ca-α-SiAlON: ICSD#201683)

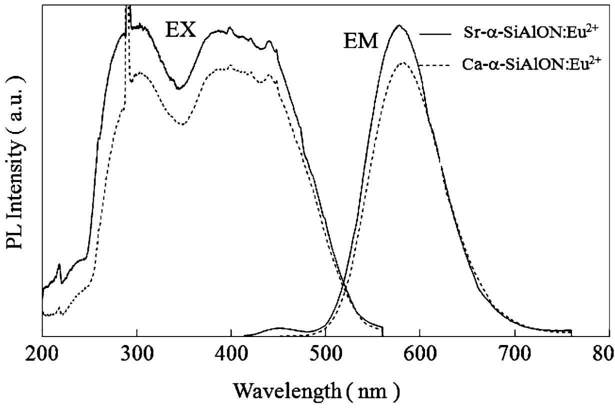

Fig. 2 Excitation and emission spectra of Sr- and Ca-α-SiAlON:Eu^{2+} samples. The emission spectrum was measured under 400 nm excitation, and the excitation spectrum was monitored at 578 nm for Sr-α-SiAlON:Eu^{2+} and 581 nm for Ca-α-SiAlON:Eu^{2+}

excitation and emission spectra of Sr-α-SiAlON:Eu^{2+} and Ca-α-SiAlON:Eu^{2+} phosphors, respectively. The excitation spectrum of Sr-α-SiAlON:Eu^{2+} phosphor covers the spectral region ranging from the UV to the visible part. Two broad excitation bands are observed with the maxima at about 288 and 399 nm corresponding to the $4f^7 \rightarrow 4f^6 5d$ transition of Eu^{2+}. The emission spectrum shows a single intense broad emission band ranging from 470 to 750 nm, which is attributable to the allowed $4f^6 5d \rightarrow 4f^7$ transition of Eu^{2+}. The characteristic Eu^{3+} luminescence which exhibits sharp and line shaped spectrum between 560 and 630 nm was not observed. This suggests that the europium ion in α-SiAlON phosphor is mainly in the divalent state. A very weak emission band centered at 450 nm is probably ascribed to the luminescence of SrSi$_6$N$_8$:Eu^{2+} [17].

The emission peak wavelength of Sr-α-SiAlON:Eu^{2+} is 578 nm, which is slightly shorter than that of Ca-α-SiAlON:Eu^{2+} (581 nm). These results are comparable to the previous report [15]. It is believed that the long wavelength emission is attributed to covalent chemical bonding and a large crystal-field splitting effect on Eu^{2+} 5d band due to the presence of coordinating nitrogen [18]. Since the excitation spectra are so similar in shape for Sr-α-SiAlON:Eu^{2+} and Ca-α-SiAlON:Eu^{2+} (Fig. 2), it suggests that the covalency of Eu$_M$-N/O ($M = $ Sr, Ca) bonding and the crystal field splitting of the excited 5d levels of Eu^{2+} have almost the same values, as a result the shorter emission wavelength of Sr-α-SiAlON:Eu^{2+} could be mainly ascribed to the composition and the smaller Stokes shift (4921 and 5011 cm^{-1} for Sr- and Ca-α-SiAlON:Eu^{2+}, respectively).

Figure 3 shows the emission intensity as a function of the Eu^{2+} concentration for Sr- and Ca-α-SiAlON host lattices. For both α-SiAlONs, the emission intensity reaches a maximum at the Eu^{2+} concentration of $x = 0.02$ and then slightly decreases at high Eu^{2+} concentration originated from the concentration quenching. It is well known that the probability of energy transfer between two activator ions is inversely proportional to the nth power of R' ($n = 6$, 8, or 10), where R' is the distance between the activator ions [19]. The concentration quenching is mainly caused by the energy transfer among Eu^{2+} ions, and the probability of which increases with the concentration of Eu^{2+} increasing. When the concentration of Eu^{2+} increases, the distance between Eu^{2+} ions is small, and thus the probability of energy transfer increases. It suggests that the concentration quenching is influenced by the host lattice. As reported previously, the lattice constants of Sr-α-SiAlON are comparable to those of Ca-α-SiAlON, because the displacement of N2 sites parallel to the c axis (Fig. 4) mainly allows the interstices in α-SiAlON host lattice to accommodate the

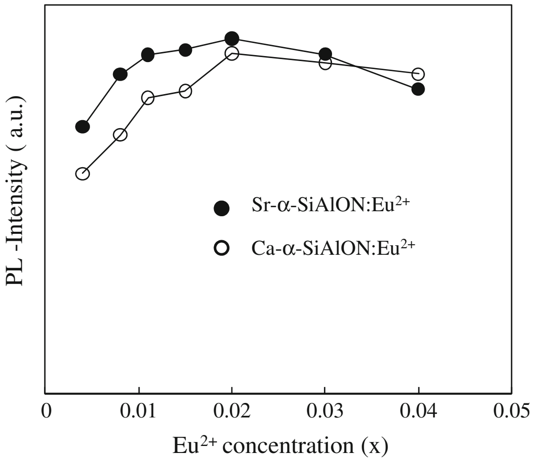

Fig. 3 Photoluminescence intensity of Sr- and Ca-α-SiAlON:Eu^{2+} phosphors as a function of the Eu^{2+} concentration

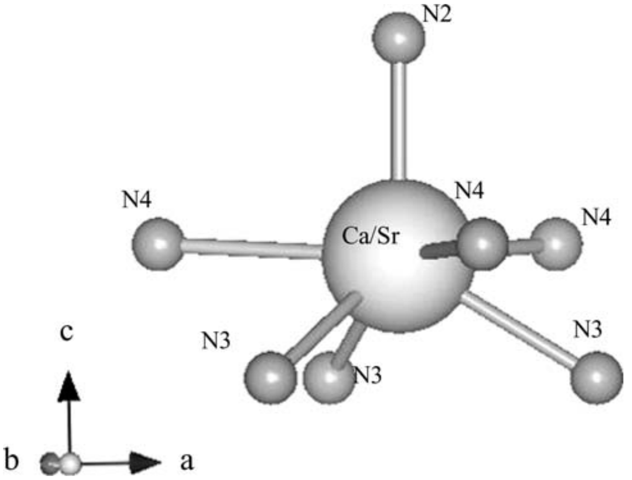

Fig. 4 The local structure of the M(Ca or Sr) site in the α-SiAlON structure

introduction of large Sr ion without significantly changing the lattice constants [15]. It indicates that the influence of the host lattice on the concentration quenching of Sr-α-SiAlON:Eu^{2+} is consistent with that of Ca-α-SiAlON:Eu^{2+}.

Thermal stability of Sr-α-SiAlON:Eu^{2+}

Figure 5 shows the thermal stability of Sr- and Ca-α-SiAlON:Eu^{2+} phosphors. It is observed that the thermal stability of Sr-α-SiAlON:Eu^{2+} phosphor is quite high that is comparable to that of Ca-α-SiAlON:Eu^{2+} phosphor. The residual emission intensity of Sr-α-SiAlON:Eu^{2+} phosphor at 300 °C is still as high as 74% of the initial intensity at room temperature, whereas it is only 26% for a standard YAG:Ce^{3+} (P46-Y3) phosphor. Such a good thermal stability of Sr- and Ca-α-SiAlON:Eu^{2+} phosphors can improve the brightness of white-LEDs of high conversion efficiency at high junction temperatures. It can be explained by thermal active phonon-assisted excitation from low to high energy sublevels in the excited states of Eu^{2+} [20]. To further understand the temperature dependence of photoluminescence intensity and to determine the activation energy for thermal quenching, the thermal quenching data were fitted by the Arrhenius equation, as shown in Fig. 6. According to the classical theory of thermal quenching, the temperature-dependent emission intensity can be described by the following equation [21]:

$$I(T) = \frac{I_0}{1 + A\exp\left(\frac{-\Delta E}{k_B T}\right)} \tag{2}$$

where I_0 is the initial intensity, $I(T)$ is the intensity at given temperature T, A is a consistent, ΔE is the activation energy for thermal quenching, and k_B is Boltzmann's constant. Figure 6 plots $\ln[(I_0/I) - 1]$ versus $1/(k_B T)$ and gives a straight line up to 300 °C. The obtained activation energy (ΔE) of Sr- and Ca-α-SiAlON:Eu^{2+} phosphors are 0.202 and 0.20 eV, respectively. As reported previously [22], the m value significantly affects the thermal quenching of α-SiAlON due to the obvious lattice expansion. In this case, the lattice constants of Sr-α-SiAlON:Eu^{2+} are almost comparable to those of Ca-α-SiAlON:Eu^{2+} because of the displacement of N2 sites along to c-axis [15], as mentioned above. It is then suggested that the thermal quenching of Sr- and Ca-α-SiAlON:Eu^{2+} phosphors with the same Eu^{2+} concentration are fixed by the network of (Si, Al)–(O, N) in α-SiAlON and nearly independent of the local structure around Sr (Eu^{2+}) or Ca (Eu^{2+}) ions. In addition, the shift of the emission band of Sr-α-SiAlON:Eu^{2+} with increasing temperature is negligible (see Fig. 7). These experimental results show that Sr-α-SiAlON:Eu^{2+} phosphor is a good yellow phosphor candidate for creating white light when combined with high-power blue-LED chips.

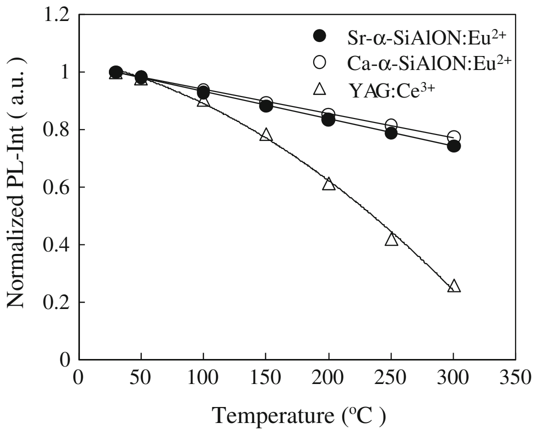

Fig. 5 Temperature dependence of PL intensity of Sr- and Ca-α-SiAlON:Eu^{2+} phosphors

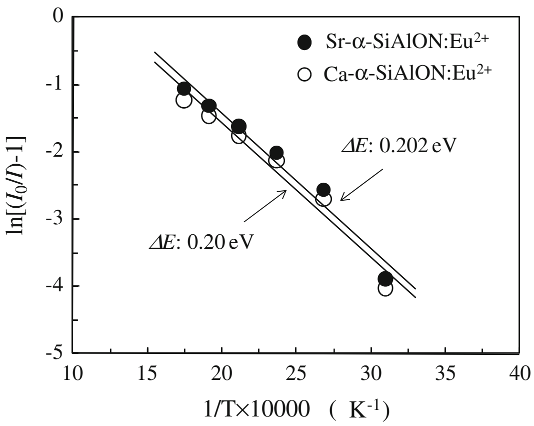

Fig. 6 Activation energy for thermal quenching of Sr- and Ca-α-SiAlON:Eu^{2+} phosphors

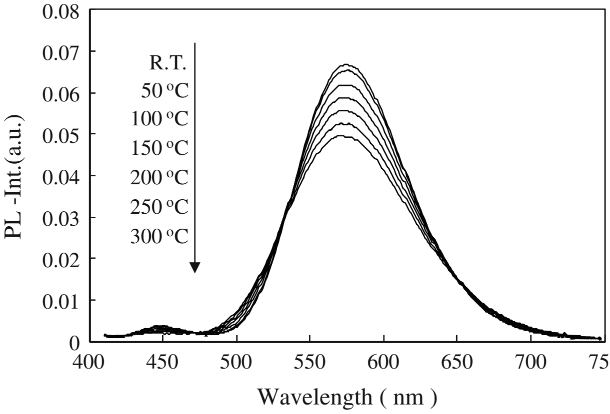

Fig. 7 Temperature dependence of emission spectra of Sr-α-SiAlON:Eu^{2+} phosphor

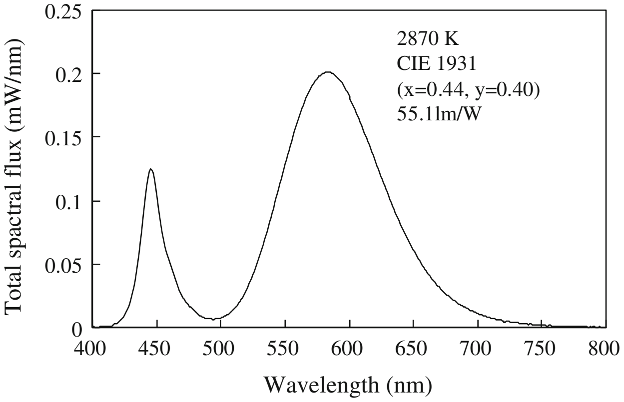

Fig. 8 Emission spectra of white-LEDs using a single Sr-α-SiAlON:Eu^{2+} phosphor

Application in white-LEDs

As Sr-α-SiAlON:Eu^{2+} exhibits very similar excitation and emission spectra with Ca-α-SiAlON:Eu^{2+}, it is thus expected that warm white-LEDs can also be realized by combining a single Sr-α-SiAlON:Eu^{2+} phosphor with a blue-LED chip. Figure 8 shows the emission spectrum of the obtained white-LEDs of Sr-α-SiAlON:Eu^{2+} phosphor with a combination of a blue-LED chip (445 nm). The spectrum was measured under a forward-bias current of 20 mA at room temperature. The CIE 1931 chromaticity (x, y) of the white-LEDs is (0.44, 0.40) with a correlated color temperature 2,870 K (warm white). The luminous efficiency is 55.1 lm/W, which is two to three times higher than that of currently used incandescent lamps.

Conclusions

Sr containing α-SiAlON phosphor ($Sr_{0.375-x}Eu_xSi_{12-m-n}Al_{m+n}O_nN_{16-n}$: $m = 0.75$, $n = x$) was obtained as a major phase in compositions with small m and n values, by firing the powder mixture of $SrSi_2$, α-Si_3N_4, AlN, and Eu_2O_3 at 2,000 °C for 2 h under 1 MPa nitrogen atmosphere. The emission wavelength of Sr-α-SiAlON:Eu^{2+} was slightly shorter than that of Ca-α-SiAlON:Eu^{2+} because of the different compositions and a small Stokes shift. The highest emission intensity was obtained at the same Eu^{2+} concentration of $x = 0.02$ for Sr- and Ca-α-SiAlON:Eu^{2+} phosphors. The residual emission intensity of Sr-α-SiAlON:Eu^{2+} phosphor at 300 °C was still as high as 74% of the initial intensity at room temperature, which was comparable to that of Ca-α-SiAlON:Eu^{2+} phosphor. It is addressed that the thermal quenching of Sr- and Ca-α-SiAlON:Eu^{2+} phosphors with the same Eu^{2+} concentration is only related to the network of (Si, Al)–(O, N) in α-SiAlON and nearly independent of the local structure around Sr (Eu^{2+}) or Ca (Eu^{2+}) ions. A warm white-LEDs with a luminous efficiency of about 55.1 lm/W and a color temperature 2,870 K was obtained using Sr-α-SiAlON:Eu^{2+} phosphor. It is expected that the Sr-α-SiAlON:Eu^{2+} phosphor can also be a good wavelength-conversion yellow phosphor for use in white-LEDs based on a blue (Ga, In)N chip.

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