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ARTICLE

Effect of replacement of Al-O for Si-N on the properties of $\text{Sr}_6\text{Si}_{25.6}\text{Al}_{6.4}\text{N}_{41.6}\text{O}_{4.4}:\text{Eu}^{2+}$ Phosphors for White Light-Emitting Diodes

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Abstract: Oxynitride phosphors $\text{Sr}_6\text{Si}_{25.6-x}\text{Al}_{6.4+x}\text{N}_{41.6-x}\text{O}_{4.4+x}:\text{Eu}^{2+}$ are synthesized by gas pressure sintering of powder mixture of SrCO_3 , AlN , Si_3N_4 and Eu_2O_3 at 1800 °C and 0.5 MPa of N_2 for 10 h, and their photoluminescence properties are investigated. $\text{Sr}_6\text{Si}_{25.6-x}\text{Al}_{6.4+x}\text{N}_{41.6-x}\text{O}_{4.4+x}:\text{Eu}^{2+}$ can be excited efficiently over a broad spectral range between 300 and 500 nm, and exhibit an intense green emission centered at about 515 nm with a full width at half maximum of 65 nm due to the $4f^65d^1-4f^7$ transition of Eu^{2+} ions. The influence of the replacement of Si-N by Al-O on luminescence properties and crystal structure is reported in a series of $\text{Sr}_6\text{Si}_{25.6-x}\text{Al}_{6.4+x}\text{N}_{41.6-x}\text{O}_{4.4+x}:\text{Eu}^{2+}$ phosphors. Different Sr sites are found in the crystal structure. The thermal quenching property of the green phosphors is better than that of typical orthosilicate $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ phosphor. The interesting photoluminescence properties indicate that the $\text{Sr}_6\text{Si}_{25.6}\text{Al}_{6.4}\text{N}_{41.6}\text{O}_{4.4}$ phosphor a promising green emitting candidate for white LEDs applications.

White light-emitting diodes(LEDs) converted by phosphors have gained significant commercial interest due to their extraordinary luminous efficiency, long lifetime, low power consumption and free of toxic mercury, which are supposed to replace the traditional incandescent and fluorescent tubes and suitable for backlight and medical applications^[1-4,26]. The most common way to create a white LED is to combine a blue InGaN chip with YAG: Ce yellow phosphors^[5-6], which cannot fully meet the requirements for LED applications due to the poor color rendering and high color temperature according to the color deficiency in red and green spectral range. Extensive efforts have been made to find alternative phosphors during the last few years. Novel nitride and oxynitride compounds have been synthesized as host materials, and become important wavelength-conversion phosphors for use in white-LEDs when doped with rare earth ions due to their strong absorption in the near-UV and blue spectral range. Higher thermal and chemical stabilities of the nitride and oxynitride phosphors are observed due to their stiff frameworks in the host lattices interconnected by $[\text{SiN}_4]$ tetrahedrons^[7-8]. Nitride/oxynitride hosts activated with Eu^{2+} such as red-emitting $\text{M}_2\text{Si}_5\text{N}_8$ ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$)^[9-10,27], MAiSiN_3 ($\text{M}=\text{Ca}, \text{Sr}$)^[11-12], orange-red $\text{SrAlSi}_4\text{N}_7$ ^[13], yellow-emitting $\text{Ca}-\alpha\text{-SiAlON}$ ^[14], and greening-emitting MYSi_4N_7 ($\text{M}=\text{Sr}, \text{Ba}$)^[15], $\text{MSi}_2\text{O}_2\text{N}_2$ ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$)^[16], $\text{M}_3\text{Si}_6\text{O}_{12}\text{N}_2$ ($\text{M}=\text{Sr}, \text{Ba}$)^[17], $\beta\text{-SiAlON}$ ^[18-19], have been systematically investigated. Among these (oxy)nitride luminescence materials, $\beta\text{-SiAlON}:\text{Eu}^{2+}$ phosphor exhibits an intense green emission with the peak around 535 nm and a strong absorption in the range of UV to blue region. However, the efficient synthesis of the $\beta\text{-SiAlON}:\text{Eu}^{2+}$ phosphor is not facile, which should be sintered at up to 2000 °C^[19-20].

Recently, novel green or blue-green emitting Eu^{2+} activated Sr-SiAlON phosphors obtained by partial substitution of Si by Al have been developed. Some of the Oxonitridoaluminosilicates (so-called SiAlON) are isotypic to known (oxy)nitridosilicates, such as $\text{SrSiAl}_2\text{O}_3\text{N}_2$ (isotypic to LnSi_3N_5 ($\text{Ln}=\text{La}, \text{Ce}, \text{Pr}, \text{Nd}$))^[21] and $\text{Sr}_2\text{Al}_x\text{Si}_{12-x}\text{N}_{16-x}\text{O}_{2+x}$ ($x\approx 2$)^[22] (isotypic to $\text{BaSi}_6\text{N}_8\text{O}$). Composite crystals with commensurate phases are reported lately, $\text{Sr}_5\text{Si}_{21-x}\text{Al}_{5+x}\text{O}_{2+x}\text{N}_{25-x}:\text{Eu}^{2+}$ ($x\approx 0$)^[23] with the emission peak wavelength at about 510 nm and $\text{Sr}_3\text{Si}_{13}\text{Al}_3\text{O}_2\text{N}_{21}$ ^[24-25] with the emission spectrum ranging from 515 to 525 nm were synthesized, which realize highly efficient luminescence and excellent thermal stability. In this paper, $\text{Sr}_6\text{Si}_{25.6-x}\text{Al}_{6.4+x}\text{N}_{41.6-x}\text{O}_{4.4+x}:\text{Eu}^{2+}$ phosphors with different x values are synthesized via solid state reaction under N_2 atmosphere, the crystal structure of which is found out to be similar to composite Sr-containing SiAlON phases reported before, the effect of the replacement of Al-O for Si-N on the photoluminescence and thermal quenching properties is investigated.

1. Experiment

1.1 Preparation

$\text{Sr}_6\text{Si}_{25.6-x}\text{Al}_{6.4+x}\text{N}_{41.6-x}\text{O}_{4.4+x}:\text{Eu}^{2+}$ phosphors with different x values ($x=-0.15-0.60$) were synthesized at 1800 °C and 0.5 MPa under N_2 atmosphere. Stoichiometric amount of analytical pure raw materials of SrCO_3 (Rare metallic, 99.99%), Si_3N_4 (Sigma-Aldrich, >99%), AlN (Tokuyama, >99%), Eu_2O_3 (Aldrich Chemical, >99%) and SiO_2 (Admafine, 99.8%) were weighed and mixed in an agate mortar. The mixed powder was placed in a tungsten crucible and heated in a graphite resistance furnace from room temperature to 1800 °C over a period of 6 h with a

heating preservation time of 10 h in the graphite resistance furnace. The powder after sintering was cooled down to room temperature in the furnace. The chilled products were grounded for further measurements.

1.2 Characterization

The phase purity of all samples were identified by the X-ray powder diffraction (XRD, Advanced D8, Bruker, Cu K α , $\lambda=0.15418$ nm) in the 2θ range of 10° - 45° . Measurement of photoluminescence properties and reflectance spectra in the UV and visible range were carried out on a UV-Vis spectrophotometer (Horiba Scientific, FluoroMax-4, USA) using a 200 W Xe-lamp as excitation source. The temperature dependence PL spectra were tested (25 - 200°C) by a spectrophotometer equipped with homemade graphite heating under the excitation at 460 nm. All measurements were accomplished at room temperature unless otherwise mentioned. External (η_0) and internal (η_i) quantum efficiencies measurement were recorded by an intensified multichannel spectrometer (QE-2100, Otsuka electronics, Japan). A white BaSO $_4$ powder was used as a standard reference for correction in the measurement of QE.

2. Results and discussion

2.1 Crystalline and structure

The Rietveld structure refinement of the composition of Sr $_6$ Si $_{25.6}$ Al $_{6.4}$ N $_{41.6}$ O $_{4.4}$: Eu $^{2+}$ is performed as shown in Fig.1. The red lines and black lines represent for the observed and calculated patterns, respectively, and are well matched with each other. The refinement parameters are also listed in the figure. The XRD patterns of Sr $_6$ Si $_{25.6-x}$ Al $_{6.4+x}$ N $_{41.6-x}$ O $_{4.4+x}$: Eu $^{2+}$ with different x values have been given in Fig.2. As can be seen from the figure, pure phases were synthesized and the diffraction patterns are well indexed. The diffraction peaks show little shift to higher angles with the increasing of x values according to the expansion of the lattice as shown in Fig.3, when there are more Si-N bonds replaced by slightly larger Al-O bonds. The variation of the lattice parameters demonstrates that the Si-N and Al-O pairs can be successfully incorporated in the Sr $_6$ Si $_{25.6}$ Al $_{6.4}$ N $_{41.6}$ O $_{4.4}$ lattice. Samples exhibit different compositions with different x values. A small amount of SrAlSiN $_7$ appeared as an impurity phase when $x \geq 0.30$ and the diffraction peaks which belonging to SrAlSiN $_7$ increase gradually with increasing x . At the meantime, it seems that Si $_3$ N $_4$ is excessive when $x \leq -0.15$ for the presence of the diffraction peaks of β -Si $_3$ N $_4$.

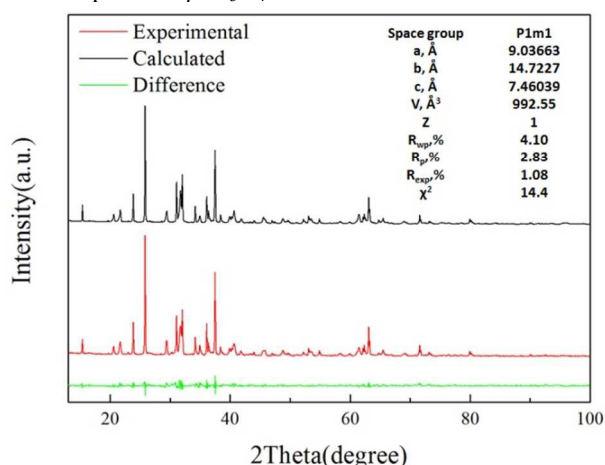


Fig.1 Rietveld refinement patterns for X-ray powder diffraction data of Sr $_6$ Si $_{25.6}$ Al $_{6.4}$ N $_{41.6}$ O $_{4.4}$: Eu $^{2+}$ phosphor

As shown in Fig.4, the crystal structure of Sr $_6$ Si $_{25.6}$ Al $_{6.4}$ N $_{41.6}$ O $_{4.4}$ was estimated to be a monoclinic structure and belonging to the space group P1m1 with the cell parameters of $a=9.03663(\text{\AA})$, $b=14.7227(\text{\AA})$, $c=7.46039(\text{\AA})$, and the unit cell volume $V=992.55(\text{\AA}^3)$. In the crystal structure, two types of channels running along the [010] crystal face are contained with three unique Sr atoms, and the coordination numbers of the sr atoms in Sr $_6$ Si $_{25.6}$ Al $_{6.4}$ N $_{41.6}$ O $_{4.4}$ are all nine. The crystallographic occupancy of Eu $^{2+}$ ions in Sr $_6$ Si $_{25.6}$ Al $_{6.4}$ N $_{41.6}$ O $_{4.4}$ was studied and verified to be the site of Sr $^{2+}$ ions. The channels cross a three-dimensional Si-Al-O-N network, [MX $_4$] (X=N, O; M=Si, Al) tetrahedrons are combined and extend along ordered layers, and the Sr and Eu atoms are contained in the channel-like voids [29].

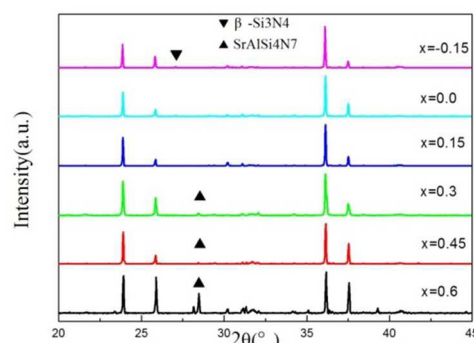


Fig.2 XRD patterns of Sr $_6$ Si $_{25.6-x}$ Al $_{6.4+x}$ N $_{41.6-x}$ O $_{4.4+x}$: Eu $^{2+}$ ($x=-0.15$ - 0.60) in the range of $2\theta=20^\circ$ - 45°

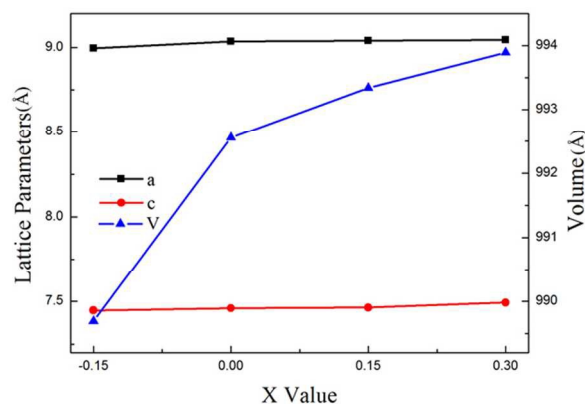


Fig.3 Variation of the cell parameters of a , b , c and volume of Sr $_6$ Si $_{25.6-x}$ Al $_{6.4+x}$ N $_{41.6-x}$ O $_{4.4+x}$: Eu $^{2+}$ ($x=-0.15$ - 0.30)

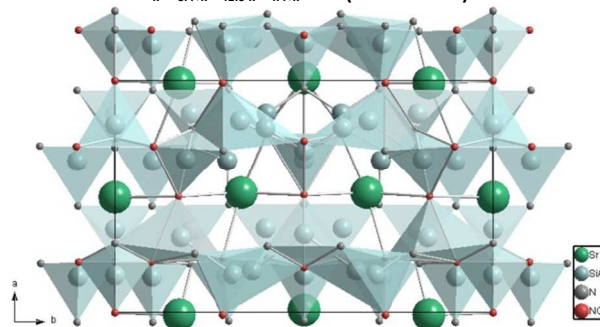


Fig.4 The schematic diagram of the crystal structure of $\text{Sr}_6\text{Si}_{25.6}\text{Al}_{6.4}\text{N}_{41.6}\text{O}_{4.4}:\text{Eu}^{2+}$ view along [001]

2.2 Luminescence properties

Photoluminescence emission, excitation and reflection spectra of $\text{Sr}_6\text{Si}_{25.6}\text{Al}_{6.4}\text{N}_{41.6}\text{O}_{4.4}:\text{Eu}^{2+}$ is shown in Fig.5. The reflection spectrum of the phosphor shows a strong absorption band covering from near UV to blue range. The emission spectra when excited by 365, 400 and 460 nm reveal slight shifts in peak wavelength which may be ascribed to the different kinds of Eu^{2+} luminescence centers for the three unique Sr types. The emission spectra under different excitation show similar features with a broad centered at about 515 nm band and the full width at half maximum (FWHM) is approximately 65 nm. It is clear that Eu are not present as trivalent ions in the phosphors ascribed to the absence of sharp f-f transition lines of Eu^{3+} in the excitation spectra, which can be inferred that the Eu^{3+} ions were reduced to divalent ones by solid state combustion under nitrogen atmosphere. The excitation spectrum of the green emission extends from 300 to 500 nm indicating that the phosphor can be efficiently excited by UV or blue light. The broad excitation band enables the Eu^{2+} doped $\text{Sr}_6\text{Si}_{25.6-x}\text{Al}_{6.4+x}\text{N}_{41.6-x}\text{O}_{4.4+x}$ phosphors to emit intense green light when combined with UV or blue LED chips. The internal and external quantum efficiencies (QE) were collected at the excitation of 460 nm, and the efficiencies come out to be 85% and 64% respectively.

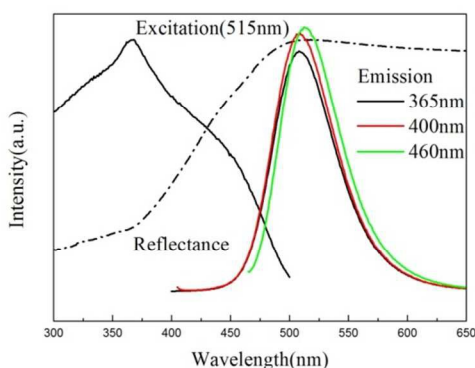


Fig.5 Excitation, reflectance and emission spectra of $\text{Sr}_6\text{Si}_{25.6}\text{Al}_{6.4}\text{N}_{41.6}\text{O}_{4.4}:\text{Eu}^{2+}$ phosphor

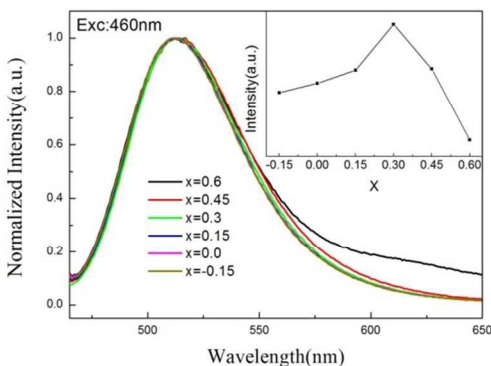


Fig.6 Normalized spectra and intensity of $\text{Sr}_6\text{Si}_{25.6-x}\text{Al}_{6.4+x}\text{N}_{41.6-x}\text{O}_{4.4+x}:\text{Eu}^{2+}$ ($x=-0.15-0.60$) phosphors

Meanwhile, normalized emission spectra of $\text{Sr}_6\text{Si}_{25.6-x}\text{Al}_{6.4+x}\text{N}_{41.6-x}\text{O}_{4.4+x}:\text{Eu}^{2+}$ ($x=-0.15-0.60$) are depicted in Fig.6. It is obviously that emission peak wavelength of all samples are nearly the same and the features of the spectra are almost similar except for relative intensity from 550 to 650 nm especially for $x \geq 0.45$. Intense green emissions extend from 470 to 550 nm with an emission peak of 515 nm are found of $\text{Sr}_6\text{Si}_{25.6-x}\text{Al}_{6.4+x}\text{N}_{41.6-x}\text{O}_{4.4+x}:\text{Eu}^{2+}$ ($x=-0.15-0.60$) phosphors when doped with a Eu^{2+} concentration of 3% mole fraction. The occurrence of an additional weak band emission in the red spectrum at about 600 nm besides the green emission band may be caused by minute contaminations of powder samples with orange-emitting $\text{SrAlSi}_4\text{N}_7:\text{Eu}^{2+}$. This is corroborated by the measurements of X-ray powder diffraction. The photoluminescence intensity is closely related to the variations of compositions of the phosphors. The inset in Fig.6 shows the emission intensity variations of $\text{Sr}_6\text{Si}_{25.6-x}\text{Al}_{6.4+x}\text{N}_{41.6-x}\text{O}_{4.4+x}:\text{Eu}^{2+}$ ($x=-0.15-0.60$) phosphors. When x value increases from -0.15 to 0.60, the relative emission intensity increases to a maximum with an x value of 0.30, and then decreases with an enhancement of the red spectrum. With the increasing of Al-O content, the crystal structure shrinks because that the Al-O bonds are shorter than Si-N, leading the decrease of the emission intensity due to the reduction of 5d energy level.

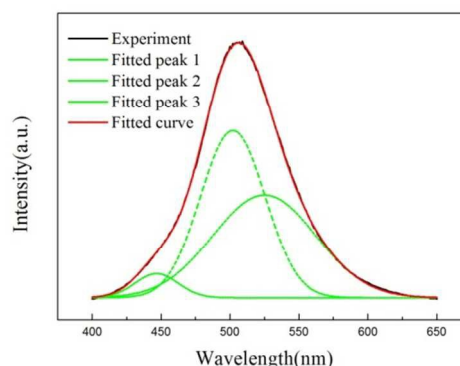


Fig.7 Decomposed emission curves by Gaussian simulation of $\text{Sr}_6\text{Si}_{25.6}\text{Al}_{6.4}\text{N}_{41.6}\text{O}_{4.4}:\text{Eu}^{2+}$

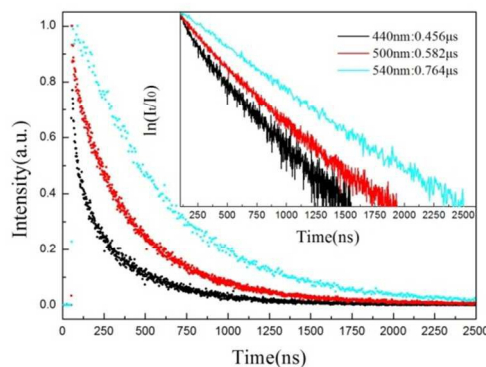


Fig.8 Decay curve and fitted curves monitored at 440, 500, 540nm and excited under 460 nm for $\text{Sr}_6\text{Si}_{25.6}\text{Al}_{6.4}\text{N}_{41.6}\text{O}_{4.4}:\text{Eu}^{2+}$

Fluorescence decay curves of $\text{Sr}_6\text{Si}_{25.6}\text{Al}_{6.4}\text{N}_{41.6}\text{O}_{4.4}:\text{Eu}^{2+}$ is depicted in Fig.8 by monitoring 440, 500 and 540 nm. The decay curves are fitted with a stretched exponential

Kohlrausch-William-Watts (KWW) function to get a more quantitative result [28]:

$$I_t = I_0 \times e^{-(t/\tau_{1/e})}$$

This function describes the exponential decaying fluorescence intensity I_t , which drops to $1/e$ of the initial intensity I_0 after the decay time $\tau_{1/e}$. The decay time monitoring 440 nm is 0.456 μ s, monitoring 500 nm is 0.582 μ s while that monitoring 540 nm is 0.764 μ s. This implies that the broad emission of $\text{Sr}_6\text{Si}_{25.6}\text{Al}_{16.4}\text{N}_{41.6}\text{O}_{4.4}:\text{Eu}^{2+}$ is come out from three individual curves ascribed to three different Sr sites in $\text{Sr}_6\text{Si}_{25.6}\text{Al}_{16.4}\text{N}_{41.6}\text{O}_{4.4}$ crystal lattice. The emission spectrum is decomposed into three bands centered at 440, 500, 540 nm by using Gaussian simulations as shown in Fig.7. The coordination numbers of the three different Sr sites are nine all, two of them are coordinated with six N atoms and three O atoms, while the other one is coordinated with five N atoms and four O atoms, as shown in Fig.9. The average distances of the [Sr-N/O] bonds are calculated to be 2.85, 2.85 and 2.98 Å. The similar interatomic distances of the [Sr-N/O] bonds and the same coordination number make the luminescence centers undistinguishable according to crystal field theory.

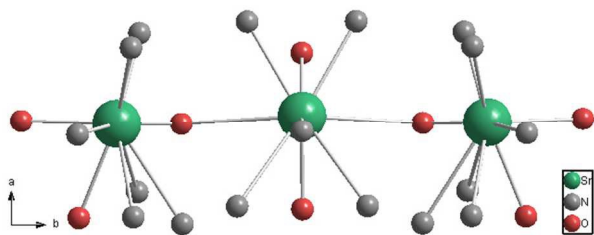


Fig.9 Sr sites with different coordination in $\text{Sr}_6\text{Si}_{25.6}\text{Al}_{16.4}\text{N}_{41.6}\text{O}_{4.4}$ crystal structure

2.3 Thermal quenching properties

To fabricate a high efficiency white LEDs, excellent temperature stability is one of the most significant technical parameters for phosphors. Thermal quenching properties of $\text{Sr}_6\text{Si}_{25.6-x}\text{Al}_{16.4+x}\text{N}_{41.6-x}\text{O}_{4.4+x}:\text{Eu}^{2+}$ ($x=0.00$ and 0.30) are investigated, and the temperature dependent emission spectra of the phosphors are shown in Fig.10. The intensity of the emission spectra decreases gradually when the phosphors are heated from room temperature up to 200°C, which is caused by the thermal vibration enhancement of the crystal lattice. The residual emission intensity at 200°C are 38% and 40% of the initial intensity at room temperature for $x=0.0$ and $x=0.3$ respectively, whereas only 25% of the emission intensity is remained for that of Ba_2SiO_4 phosphor. The crystal structure of the host material is determinant to the diversity of the thermal quenching properties. The Sr-SiAlON phosphors such as $\text{Sr}_6\text{Si}_{25.6}\text{Al}_{16.4}\text{N}_{41.6}\text{O}_{4.4}$ are built up of a three-dimensional Si-Al-O-N network, and the Si and Al atoms are tetrahedral coordinated with N and O atoms forming [MX₄] tetrahedrons, which is quite different from an orthosilicate phosphor. The possibility of the non-radiative transition is reduced according to the rigid crystal structure of the host material, leading to a much smaller Stokes shift.

The thermal quenching properties of the phosphors become better in the sample of $x=0.00$ than that of $x=0.30$ seemingly, and the activation energies of thermal quenching properties are estimated to be 0.275 and 0.269 by the Arrhenius equation [30]. The decrease in thermal stability with increasing O

concentration is attributed to the increase in Stokes shift. The temperature dependent spectra exhibit common regular pattern, and slightly blue shifts of the emission peaks are observed, which may be ascribed to the increasing vibration energy level of the excited energy state. The thermal quenching property of $\text{Sr}_6\text{Si}_{25.6-x}\text{Al}_{16.4+x}\text{N}_{41.6-x}\text{O}_{4.4+x}:\text{Eu}^{2+}$ demonstrates that it would be a potential green phosphor for White LEDs.

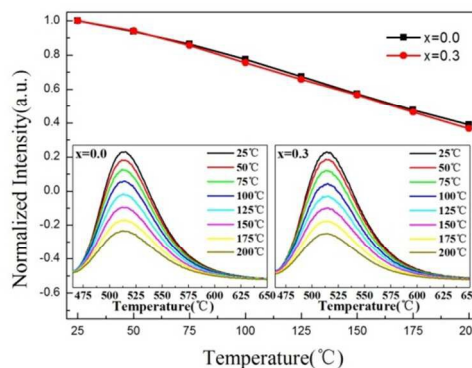


Fig.10 Temperature dependence spectra and normalized intensity of $\text{Sr}_6\text{Si}_{25.6-x}\text{Al}_{16.4+x}\text{N}_{41.6-x}\text{O}_{4.4+x}:\text{Eu}^{2+}$ ($x=0.00$ and $x=0.30$) under 460 nm excitation

2.4 CIE

The CIE chromaticity coordinates of $\text{Sr}_6\text{Si}_{25.6-x}\text{Al}_{16.4+x}\text{N}_{41.6-x}\text{O}_{4.4+x}:\text{Eu}^{2+}$ ($x=0.15-0.60$) phosphors are shown in Fig.11. The Chromaticity coordinates vary from (0.259, 0.602) to (0.353, 0.532) with various x values, which locate in yellow-green region and the shifts become slightly when $x \leq 0.30$, indicating that the chromaticity coordinates could be tuned by changing the composition of the phosphors. It is believed that the $\text{Sr}_6\text{Si}_{25.6}\text{Al}_{16.4}\text{N}_{41.6}\text{O}_{4.4}:\text{Eu}^{2+}$ could be an efficient wavelength conversion green phosphor for applications in white LEDs.

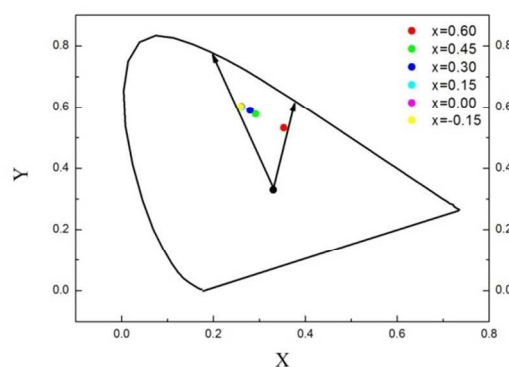


Fig.11 Chromaticity coordinates of $\text{Sr}_6\text{Si}_{25.6-x}\text{Al}_{16.4+x}\text{N}_{41.6-x}\text{O}_{4.4+x}:\text{Eu}^{2+}$ ($x=0.15-0.60$) series phosphors

3. Conclusions

Sr-containing SiAlON phosphors $\text{Sr}_6\text{Si}_{25.6-x}\text{Al}_{16.4+x}\text{N}_{41.6-x}\text{O}_{4.4+x}:\text{Eu}^{2+}$ ($x=0.15-0.60$) are synthesized by firing the powder mixture of SrCO_3 , Si_3N_4 , AlN , Eu_2O_3 and SiO_2 at 1800 °C for 10 hours at 0.5 MPa nitrogen atmosphere. An intense wavelength peaking around 515 nm with the FWHM of 65 nm is observed for $\text{Sr}_6\text{Si}_{25.6}\text{Al}_{16.4}\text{N}_{41.6}\text{O}_{4.4}:\text{Eu}^{2+}$. The reflection and

excitation spectra show a strong absorption band extending from UV to visible region. The internal and external quantum efficiencies (QE) are 85% and 64%. The emission spectrum can be decomposed to three bands centered at 440, 500, 540 nm by Gaussian simulations. Fluorescence decay curves monitoring 440, 500 and 540 nm are depicted, and the decay times are estimated to be 0.456, 0.582 and 0.764 μ s respectively, illustrating that there are three unique Sr sites in the crystal structure as reported. The emission intensity decreases to nearly 40% of the initial intensity at room temperature when measured at 200 °C, the thermal quenching effect is stronger with a lower O concentration due to a smaller Stokes shift. A slight blue shift is observed with the temperature increased which is ascribed to the increase vibration energy level of the excited electronic state. The photoluminescence properties and thermal stability demonstrate that the Sr-containing SiAlON a potential candidate for phosphor converted white LEDs.

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Notes and references

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Table of Contents Graphic

Novel oxynitride Sr-containing Sialon phosphor was synthesized, intense green emission was found and crystal structure was discussed.

