Low-pressure preparation of Eu-Doped (Sr/Ca)AlSiN$_3$ with Li$_3$N flux and its thermal quenching properties

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Nitride/nitrogen oxides are widely used in the phosphor-converted white light emitting diodes (w-LEDs) as the orange-red phosphor to improve the color-rendering index. Recently, several oxides and oxygen-free nitride phosphors are being investigated for w-LEDs. Due to the high luminous efficacy, excellent thermal and chemical stability and broad absorption range, from UV to the green region of the electromagnetic spectrum, (Sr/Ca)AlSiN$_3$: Eu^{2+} are considered as one of the most promising red phosphors for w-LEDs applications. However, the harsh synthesis conditions such as high pressure (190 MPa) and high temperature (1900℃) hinder the application of (Sr/Ca)AlSiN$_3$: Eu^{2+} in commercial devices and research activities. We demonstrate the utilization of Li$_3$N flux to decrease the synthesis temperature and improve the crystal structure of resulting compound. The Sr$_{1-x}$Ca$_x$AlSiN$_3$: Eu^{2+} compound has been successfully synthesized by the addition of Li$_3$N flux. The synthesis temperature was reduced to 1700 ℃ and reaction was carried out at lower pressure (0.12 MPa). The crystal structure, surface morphology and detailed photoluminescence characterization have been carried out and effect of Li$_3$N content along with other parameters has been studied. In addition, thermal quenching properties of Sr$_{1-x}$Ca$_x$AlSiN$_3$: Eu^{2+} are also discussed.

1. Introduction

Phosphor-based white-light-emitting diodes (w-LEDs) are considered as a replacement of the conventional incandescent and fluorescent-based light sources due to the lower energy consumption, longer lifespan and higher efficiency. A blue LED chip with a yellow phosphor, Ce^{3+} doped yttrium aluminum garnet (YAG) yellow phosphor [1], has been applied in w-LEDs. However, the low rendering index due to the lack of red component hinders its practical utilization. The red phosphors, which can be excited by the blue light from GaN or InGaN LED chips, are required to develop the white-light LED with a high rendering index. Moreover, the silicon-based nitride phosphors are promising red phosphor candidates in w-LEDs due to their excellent chemical stability and thermal quenching properties [2]. Several nitride-based red phosphors such as Eu doped (Sr/Ca)AlSiN$_3$ (SCASN) [3-8], M$_2$Si$_5$N$_8$ (M=Ca, Sr, Ba) [9-12], Ca-and Li-α-sialons[13], SrAlSi$_4$N$_7$[14, 15] and SrLi$_2$Si$_2$N$_4$ [16] have been explored. The SCASN is considered as one of the most promising red phosphors for the w-LEDs due to its high luminous efficacy, excellent thermal and chemical stability and a wide range of absorption spectrum ranging from the UV to green region of the electromagnetic radiations. The pure CaAlSiN$_3$, without Sr-doping, can be

synthesized (at 1800 °C) but the longer emitting wavelength (λ > 650 nm) hinders its application in w-LEDs. The Sr-doping and adjusting Sr to Ca ratio of Sr in CaAlSiN3 results in desirable emitting wavelength. Furthermore, when Sr to Ca ratio increase up to 50 %,, the phase structure transforms to the SrAlSiN$_3$. However, the synthesis of SrAlSiN$_3$ requires high pressure (~190 MPa) and temperature (~ 1900 °C), which restricts the commercial application of this compound [17]. Recently, Yi-Seul Kim et al. have synthesized SCASN by the spark plasma sintering (SPS) [18] and, despite the harsh synthesis conditions, pure SrAlSiN$_3$: Eu^{2+} was not obtained. Therefore, alternative techniques should be developed to synthesize pure SCASN at feasible synthesis conditions.

The phosphors can be synthesized by flux, which results in normal synthesis conditions, excellent crystallinity and purity of the final product. Recently, a Li$_3$N flux has been demonstrated to synthesize Sr$_2$Si$_5$N$_8$: Eu^{2+} phosphor at lower synthesis temperature and resulting compound showed an improvement in the integrated emitting intensity and thermal stability [19]. The Li$_3$N is an appropriate flux for nitride phosphors due to its high melting point (845 ℃) and it can improve the synthesis conditions of SCASN. Herein, we report the utilization of Li$_3$N flux to synthesize SCASN.

2. Experimental

The $Sr_{1-x}Ca_xAlSiN_3$: Eu^{2+} samples, with Li_3N flux, were synthesized by using Sr_3N_2, Si_3N_4, AlN, Eu_2O_3 (Alfa 99.99%) and Li_3N (Alfa, 99%). The binary nitride precursor (Sr_3N_2) was prepared by heating pure strontium metal under nitrogen at 800 ℃ for 10 hours in a horizontal tube furnace. The raw materials were thoroughly mixed in the stoichiometric ratio in an N_2-filled glovebox ($O_2 <$ 0.1 ppm, H_2O < 0.1 ppm). Afterwards, the mixture was transferred into a molybdenum crucible and heat-treated at 1700 ℃ for 10 hours under 0.12 MPa N_2. The constant flow N_2 (50 ml/min) was maintained during the heat-treatment process. After the sintering reaction, the samples were cooled down to room temperature and phosphor powder was obtained. The crystal structure of phosphors was studied by powder X-ray diffraction (XRD RINT2200, Rigaku with Cu Kα radiation). The morphology of the resulting powder samples was observed by scanning electron microscopy (SEM, S-3000, Hitachi). The photoluminescence spectra (PL) were measured using fluorescent spectrophotometers (Hitachi F-7000) at room temperature and a Xe-lamp was used as an excitation source. The temperature-dependent PL properties were recorded in the temperature range of 30 ℃–175 ℃, with holding time of 5 minutes to attain thermal equilibrium. The diffuse reflectance spectra were measured by using Cary 5000 UV–vis–NIR spectrophotometer, equipped with an internal diffuse reflectance accessory.

3. Results and discussion

3.1. Synthesis process

The $SrAlSiN_3$ and $CaAlSiN_3$ have an isotypic crystal lattice structure, orthorhombic with space group Cmc21, and the unit cell volume of $SrAlSiN_3$ is 4 % larger than that of $CaAlSiN_3$: Eu^{2+} [7]. The $CaAlSiN_3$ can be synthesized at high temperature (1700 °C) under atmospheric pressure, but a synthesis of $SrAlSiN_3$ cannot be achieved at atmospheric pressure to high reaction energy. During the firing process, the AlN evaporation is one of the biggest challenges and the evaporation takes place from closed crucible as well (Fig. 1). To prevent AlN evaporation, the presence of high pressure and closure of Mo crucible are key factors. To overcome this issue, we have utilized Li_3N flux and varied the Ca/Sr ratio to attain $SrAlSiN_3$–like structure.
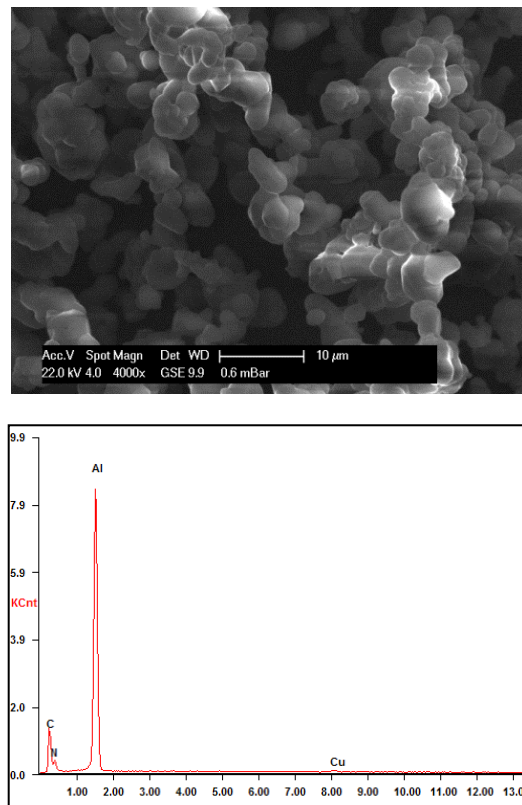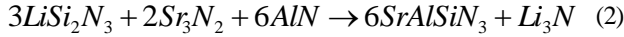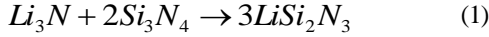

Fig. 1. SEM image and EDS analysis of evaporation in the preparation of $SrAlSiN_3$

3.2. Structure and morphology

The XRD patterns of $Sr_{0.7}Ca_{0.3}AlSiN_3$ phosphors, with 0.8 and 2.3 wt. % Li_3N, are shown in Fig. 2. It can be readily observed that the $SrAlSiN_3$ phase was successfully synthesized in the presence of 0.8 wt % Li_3N. However, a few impurity phases such as aluminum nitride (AlN) and some unidentified phases were also observed. Therefore, we have increased the Li_3N content to 2.3 wt % and observed a remarkable decrease in the impurity phases. The pure $Sr_{0.7}Ca_{0.3}AlSiN_3$ phosphor, without any residual AlN, was obtained in the presence of 2.3 wt % Li_3N. Fig. 3 presents the XRD patterns of as prepared $Sr_{1-x}Ca_xAlSiN_3$:Eu^{2+} (x = 0, 0.1 and 0.2) in presence of 2.3 wt % Li_3N. The $Sr_{1-x}Ca_xAlSiN_3$ phase can be synthesized at relatively lower pressure (~ 0.12 MPa) with Li_3N flux. Moreover, the pure $SrAlSiN_3$, without Ca substitution, was also prepared, with a small amount of residual AlN phase. Hence, it can be concluded that the addition of Li_3N flux has a significant effect on $SrAlSiN_3$ phase synthesis and the reaction pressure was remarkably decreased in the presence of Li_3N flux.

The equation 1 explains that the role of Li_3N during heat-treatment is beyond flux and it acts as a catalyst, participating in the reaction, to produce $LiSi_2N_3$ by reacting with Si_3N_4 at 1200 °C [19-22]. The $LiSi_2N_3$ and SCASN are isostructural [23] and further reaction between

LiSi$_2$N$_3$ and Sr$_3$N$_2$ results in the formation of SrAlSiN$_3$ (Equation 2). It is worth mentioning that the detailed mechanism of SrAlSiN$_3$ synthesis in the presence of Li$_3$N should be further studied and beyond the scope of this paper.

$$Li_3N + 2Si_3N_4 \rightarrow 3LiSi_2N_3 \qquad (1)$$

$$3LiSi_2N_3 + 2Sr_3N_2 + 6AlN \rightarrow 6SrAlSiN_3 + Li_3N \quad (2)$$

The SEM images of Sr$_{1-x}$Ca$_x$AlSiN$_3$: Eu^{2+} with 2.3 wt % Li$_3$N are presented in Fig. 4. The particle size has shown a direct relationship with the amount of Ca (x). Furthermore, the grain size ranges from 10 µm to 25 µm and does not show the uniformity. We have not observed any impurities during SEM imaging.
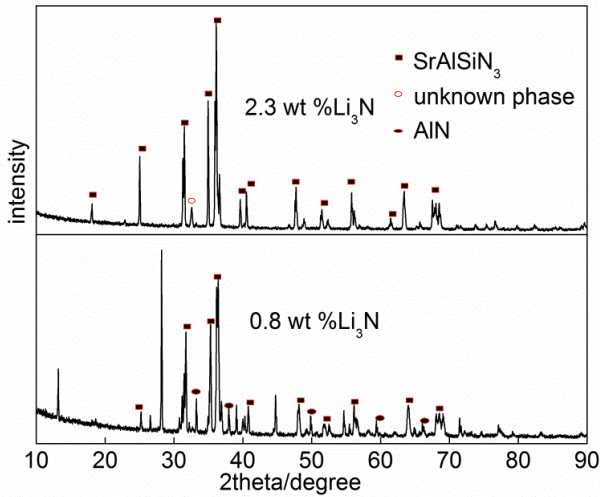

Fig. 2. The XRD patterns of as prepared
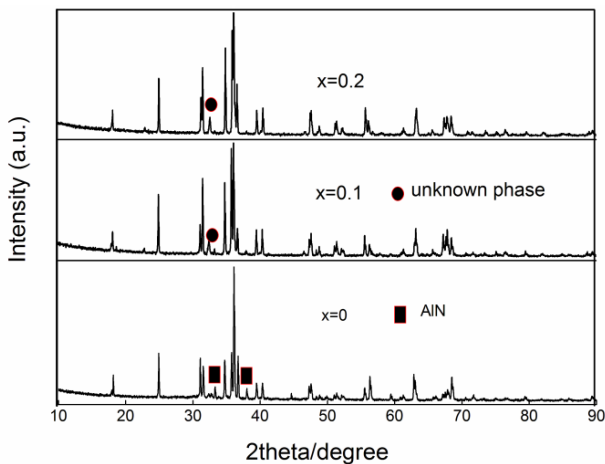SrAlSiN$_3$: Eu^{2+} with 0.8 wt. % and 2.3 wt % Li$_3$N

Fig. 3. The XRD patterns of as prepared
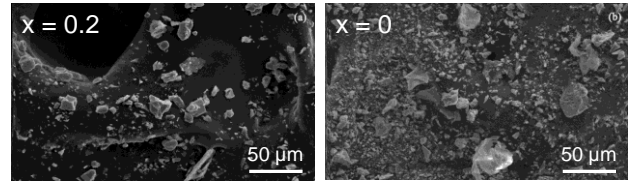Sr$_{1-x}$Ca$_x$AlSiN$_3$:Eu^{2+} (x = 0, 0.1 and 0.2) with 2.3 wt % Li$_3$N flux

Fig. 4. The SEM images of as-prepared Sr$_{1-x}$Ca$_x$AlSiN$_3$: Eu^{2+}
with 2.3 wt % Li$_3$N; (a) x = 0.2 and (b) x = 0

3.3. Photoluminescence properties

The effect of Li$_3$N flux addition on photoluminescence properties were also been studied. Fig. 5 presents the excitation and emission spectra of Sr$_{0.685}$Ca$_{0.3}$Eu$_{0.015}$AlSiN$_3$:xLi$_3$N, where x = 2.3 wt %, 1.7 wt %, or 1.05 wt %. The emission and excitation spectra in Fig. 5 were attributed to the 4f−5d transition of Eu^{2+}. The emission intensities were raised by increasing x amount. We have seen an improvement in the PL properties by Li$_3$N flux addition in precursors. The highest emission intensities were observed at x = 2.3 wt %. The improvement of the luminescent properties can be attributed to the absence of impurity phase and presence of crystalline structure due to the Li$_3$N flux addition. The excitation and emission spectra of the obtained Sr$_x$Ca$_{1-x}$Eu$_{0.01}$AlSiN$_3$ phosphors, prepared with 2.3 wt % Li$_3$N flux addition is shown in Fig. 6. The excitation and emission spectra have a blue shift with the increase of Sr content. Moreover, the Stokes shift has shown a little effect on Ca/Sr content variation (2450~2700 cm^{-1}) due to the simultaneous shift of excitation and emission spectra. The luminescence of phosphor is due to the 5d→4f transition of Eu^{2+}, which can be significantly affected by the strength of crystal-field splitting [24]. The smaller cation substitution increases crystal-field splitting strength. Therefore, the emission spectra of the Sr$_x$Ca$_{1-x}$Eu$_{0.01}$AlSiN$_3$ phosphor can be tuned by varying Sr/Ca ratio.
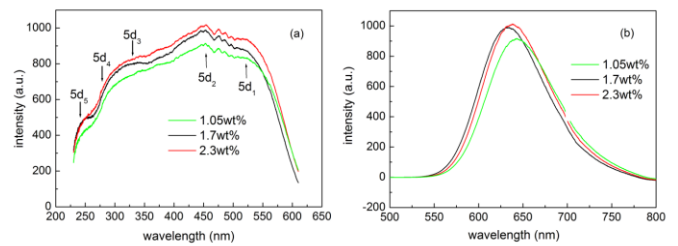

Fig. 5. The excitation and emission spectra of
Sr$_{0.685}$Ca$_{0.3}$Eu$_{0.015}$AlSiN$_3$:xLi$_3$N phosphors, where
x = 2.3 wt %, 1.7 wt % and 1.05 wt %. (λ_{ex} = 460 nm
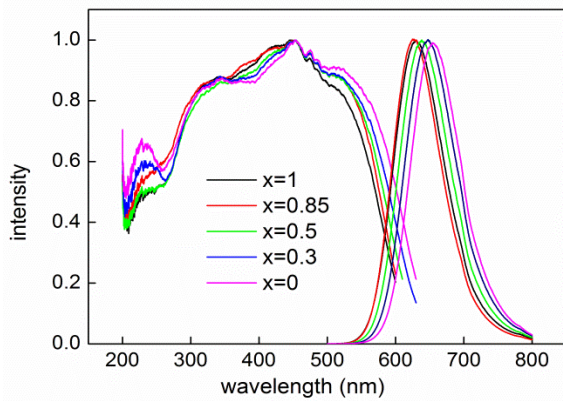and λ_{em}= 643 nm)

Fig. 6. The excitation and emission spectra of $Sr_xCa_{1-x}Eu_{0.01}AlSiN_3$ phosphors prepared with 2.3 wt % Li_3N flux

3.4. Thermal quenching properties

The thermal quenching is an important aspect of phosphor's properties in w-LEDs. The relative PL intensity of $Sr_{0.85}Ca_{0.15}Eu_xAlSiN_3$, prepared with 2.3 wt % Li_3N flux, as a function of temperature is presented in Fig. 7. The relative PL intensity has shown an inverse relationship between temperature and Eu^{2+} concentration, which is consistent with the previous reports for $Sr_2Si_5N_8$: Eu^{2+}[25]. Fig. 8 presents the relative PL intensity of $Sr_{0.89}Ca_{0.1}Eu_{0.01}AlSiN_3$, prepared with 2.3 wt % Li_3N flux, and another nitride phosphor $Sr_{1.98}Si_5N_8$: $Eu_{0.02}$ during heating and cooling. The emission intensity decreased with an increase in temperature for both compounds. However, when the temperature was decreased to 30 °C after first heating cycle, the $Sr_{0.89}Ca_{0.1}Eu_{0.01}AlSiN_3$ has shown a 100 % recovery, whereas the emission intensity of $Sr_{1.98}Si_5N_8$: $Eu_{0.02}$ was only 99 % of the initial intensity. This implies that the $(Sr/Ca)AlSiN_3$: Eu^{2+} phosphors are more stable as compared to the $Sr_2Si_5N_8$: Eu^{2+} phosphors during heating. The working temperature in LED is over 100 ℃. Therefore the thermal stability is an important aspect of phosphors used in w-LED. These results demonstrate that $MAlSiN_3$: Eu^{2+} (M=Sr, Ca) are excellent red phosphor candidate for w-LEDs.

The emission spectra of $(Sr/Ca/Eu)AlSiN_3$ phosphor can be tuned and thermal quenching properties can be significantly affected by controlling the Sr/Ca ratio. The temperature dependence of relative integrated emission intensities of $Sr_xCa_{1-x}Eu_{0.01}AlSiN_3$ phosphors, prepared with 2.3 wt % Li_3N is presented in Fig. 9(a). It can be readily observed that the $Sr_xCa_{1-x}Eu_{0.01}AlSiN_3$ phosphors have shown outstanding thermal quenching behavior, and especially for the pure $MEu_{0.01}AlSiN_3$ (M=Ca, Sr) phosphors. Fig. 9(b) shows the diffuse reflection spectra of undoped $Sr_xCa_{1-x}AlSiN_3$ prepared with 2.3 wt % Li_3N. All synthesized compounds have shown a drop in the reflection in the UV range, around 300 nm, except $SrAlSiN_3$ (280 nm) and the estimated band gap energy of

$SrAlSiN_3$, from the reflection spectra, is higher than other compounds. The thermal quenching mechanism of Eu^{2+} 5d →4f luminescence can be attributed to ionization of 5d electrons to the conduction band [26] and the larger band gap exhibits lower thermal quenching. This might be the reason for excellent thermal quenching properties of $SrAlSiN_3$.
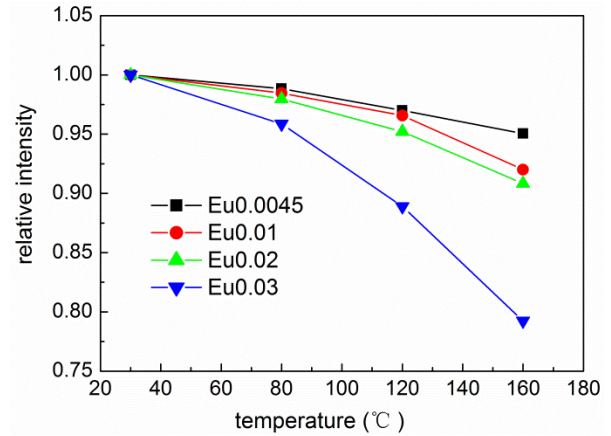

Fig. 7. The relative PL intensity of $Sr_{0.85}Ca_{0.15}Eu_xAlSiN_3$, prepared with 2.3 wt % Li_3N, as a function of heating temperature
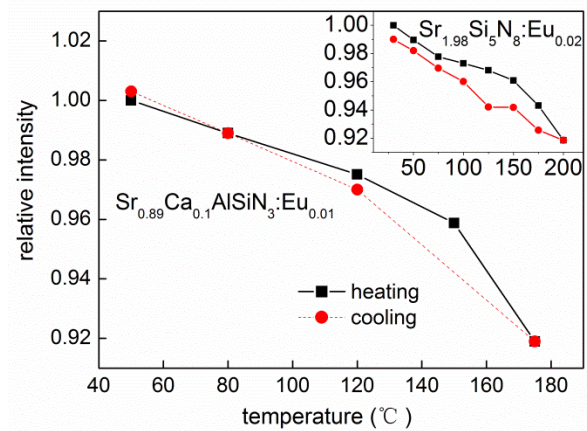

Fig. 8. Relative PL intensity of $Sr_{0.89}Ca_{0.1}Eu_{0.01}AlSiN_3$, prepared with 2.3 wt % Li_3N, and $Sr_{1.98}Si_5N_8$: $Eu_{0.02}$ (internal) as a function of temperature in heating and cooling cycle
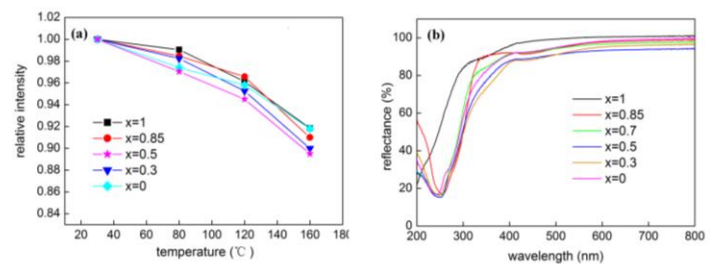

Fig. 9. (a)The relative PL intensity of $Sr_xCa_{1-x}Eu_{0.01}AlSiN_3$, prepared with 2.3 wt % Li_3N, as a function of heating temperature; (b)The diffuse reflection spectra of $Sr_xCa_{1-x}AlSiN_3$ prepared with 2.3 wt % Li_3N

4. Conclusions

The effect of Li_3N flux on synthesis conditions, crystal structure, morphology and photoluminescence properties of $(Sr/Ca)AlSiN_3$: Eu^{2+} has been explored and the thermal quenching properties of the as-prepared samples are discussed. By using Li_3N flux, the $SrAlSiN_3$: Eu^{2+} can be synthesized at atmospheric pressure and improved photoluminescence properties can be obtained. The Li_3N flux improves the reaction activity and provides abundant N ions for the reaction, which results in the formation of $SrAlSiN_3$ at atmospheric pressure. The excellent photoluminescence and thermal quenching resistant properties of $SrAlSiN_3$: Eu^{2+} indicate that it is an outstanding candidate as a red phosphor in w-LEDs.

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