

Preparation and Photo luminescent Properties of $\text{Sr}_2\text{Si}_5\text{N}_8$: Eu^{2+} Red Phosphors for White Light-Emitting Diodes

Zhibin Yu, ShiQing Man*, Pan He, Ning Zhang, Ciyong Gu

Yunnan Key Laboratory for Optoelectronic Information Technology, School of Physics and Electronic Information, Yunnan Normal University, Kunming 650500, China

*Corresponding author: man_shiqing@163.com

Abstract. This paper study a simple, inexpensive synthetic route to $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ based red nitride phosphors for white light-emitting diodes (WLEDs). The Eu^{2+} doped $\text{Sr}_2\text{Si}_5\text{N}_8$ nitride phosphor were synthesized by carbothermal reduction and nitridation method using SrCO_3 , Si_3N_4 and Eu_2O_3 as raw materials, and carbon as main reduction agent. $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphors was obtained at 1600°C under N_2 atmosphere. $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphors structure were investigated using X-ray diffraction (XRD); the phosphors excitation spectrum, emission spectrum and decay lifetime were obtained by fluorescence spectrophotometer. Excitation spectrum of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphors showed a broad excitation bands peaking at 332 nm by both UV and blue light. There is an asymmetric wide emission peaks between 500 nm and 750 nm originated from the $4f^65d^1-4f^7$ transitions of Eu^{2+} ion. And the lifetime of Eu^{2+} in the $\text{Sr}_2\text{Si}_5\text{N}_8$ host is 1919.81 ns. The CIE chromaticity coordinates of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphors are (x=0.5549, y=0.4316).

1. Introduction

White light-emitting diodes (WLEDs) have attracted substantial attention in recent years for applications in solid-state lighting [1]. WLEDs have marked advantages over the traditional incandescent and fluorescent lamps, such as superior lifetime, higher brightness, lower energy consumption and better reliability [2]. Therefore, WLEDs have been considered to be promising candidates for the next generation of lighting sources. The WLEDs could be generated by combining the blue emission of InGaN diode chip with the yellow luminescence from $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG: Ce^{3+}) phosphors [3, 4]. However, this white light has a low color rendering index (CRI) because the white light lacks sufficient red emission, which has limited the applications of WLEDs in indoor lighting and display devices. In order to obtain a high color rendering, there are alternative ways to generate warm white lights with a red component: one is to compensate the red deficiency of YAG: Ce^{3+} based WLEDs with an additional red phosphors [5], and another is to combine an ultraviolet (UV) chip with red, green, and blue-emitting (RGB) phosphors [6]. For both methods, red phosphors which can be efficiently excited by InGaN LED chip at blue and UV region are in great demand. Unfortunately, the efficiency of currently commercially used red phosphors is much lower than that of green and blue phosphors. For both approaches, in order to obtain high-quality warm white light output, more efforts should be devoted to searching for efficient red phosphors [7, 8].



In recent years, SiN_4 -base nitride phosphors with red emission including nitridosilicates, nitridoaluminosilicates and other nitrides, etc., have been extensively studied as red phosphors for WLEDs, such as $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ and $\text{MAlSiN}_3:\text{Eu}^{2+}$ ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$) [9–17]. Among these phosphors, $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ has demonstrated high luminescence intensity and very low thermal quenching. Several approaches have been tried for preparation of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphors, including a traditional solid-state reaction method using nitride raw materials and a reaction between metals and silicon diimide $\text{Si}(\text{NH})_2$ [18]. These materials are not only expensive but also very sensitive to oxygen and moisture. $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphors can be directly prepared by a synthetic route using SrCO_3 , Eu_2O_3 , and Si_3N_4 as raw materials. However, the resultant product was a complex mixture of $\text{Sr}_2\text{Si}_5\text{N}_8$ and Sr_2SiO_4 [19]. Therefore, a simple, efficient method is needed to synthesize $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ red phosphors with pure-phase and excellent luminescence properties.

In this work, using SrCO_3 , Eu_2O_3 , and Si_3N_4 as the raw material and carbon as reduction agent to synthesize $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphors. All the raw materials used were commercially available, used low cost oxides, and the synthesis in a N_2 atmosphere. The photoluminescence properties and structure of obtained $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphors were investigated.

2. Experimental

2.1. Sample Preparation

The Eu^{2+} doped $\text{Sr}_2\text{Si}_5\text{N}_8$ nitride phosphors were synthesized by carbothermal reduction and nitridation method. The raw materials using SrCO_3 (99.9%), Si_3N_4 (99.9%) and Eu_2O_3 (99.99%), and carbon (99.9%, $n_{\text{C}}/n_{\text{Si}}=1.5$) as main reduction agent, using NH_4Cl (99.5%, 4 wt %) as a flux. They were stoichiometric ally weighed and mixed thoroughly in an agate mortar. Then mixtures transferred into a graphite/alumina/corundum crucible placed into a tubular furnace. The furnace chamber was pumped down to high vacuum and filled with pure N_2 , and a flow rate of 1 L/min was maintained during the heating process. Hereafter the mixed raw materials were fired at 1600°C for 3 h under nitrogen atmosphere. After firing, the obtained phosphors were cooled to room temperature in a furnace under a continuous flow of N_2 gas. Then polish in an agate mortar to form the final products.

2.2. Characterization

The crystal structure of the as-synthesized powder was inspected with an X-ray powder diffraction (XRD, Rigaku Ultima IV), which enabled average depiction of the structure through pattern matching, using $\text{Cu K}\alpha$ radiation ($\lambda=0.154056$ nm) at room temperature. Accelerating voltage is 40 kV, Emission current is 40 mA. The data were collected over the 2θ range of 10 – 80° . The step width was 0.02° and the scanning speed was $15^\circ/\text{min}$. The photoluminescence excitation and emission spectrum were measured at room temperature using a fluorescent spectrophotometer (Spectrofluorometer FS 5, United Kingdom) with a 500 W Xenon lamp as an excitation source. And the decay curve of the powder were measured at room temperature using a fluorescent spectrophotometer (Spectrofluorometer FS 5, United Kingdom) with a 500 W Microsecond Flash lamp as an excitation source. All spectra were collected at room temperature under same experimental conditions.

3. Results and Discussion

3.1. Structure Analysis of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ Phosphors

Figure 1 shows the XRD pattern of $\text{Sr}_{2-x}\text{Si}_5\text{N}_8:\text{Eu}_x^{2+}$ ($x=0.02$) phosphors samples prepared at 1600°C for 3 h. Through the comparison with the standard card of $\text{Sr}_2\text{Si}_5\text{N}_8$ (PDF card no. 85-0101), it can be seen in Figure 1 that samples are consisted by pure $\text{Sr}_2\text{Si}_5\text{N}_8$ phase and no apparent impurity phases were found. Illustrate that the Eu^{2+} doped $\text{Sr}_2\text{Si}_5\text{N}_8$ samples are indexed with an orthorhombic lattice with the space group of $\text{Pmn}2_1$. Moreover, the Eu^{2+} ions are effectively doped into the host lattice. It was also indicated that a little amounts Eu^{2+} ions doped did not caused any significant change in the host structure, because the close ionic radii of Sr^{2+} (0.112 nm) and Eu^{2+} (0.117 nm) and the Eu^{2+} and

Sr^{2+} ion have the same valence, so the Eu^{2+} enter the crystal lattice mainly account the location of Sr^{2+} [20].

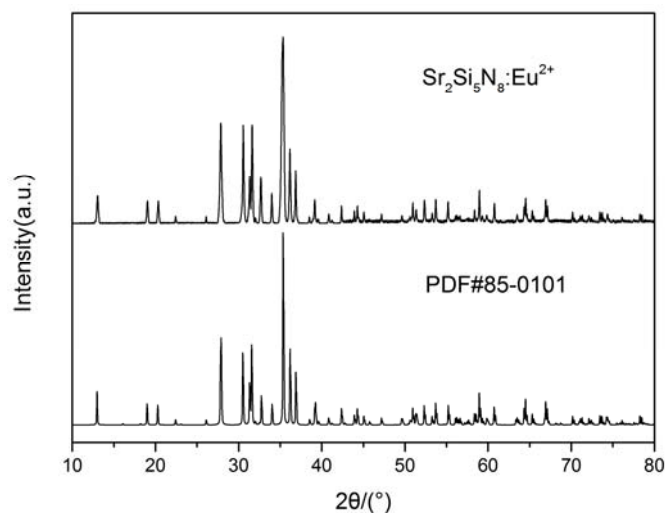


Figure 1. The XRD pattern of $\text{Sr}_{2-x}\text{Si}_5\text{N}_8:\text{Eu}_x^{2+}$ ($x=0.02$) phosphors.

3.2. Photo luminescent Properties of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ Phosphors

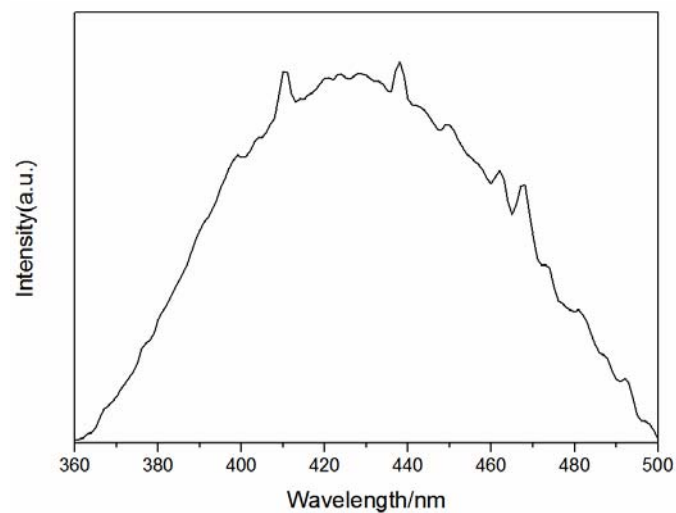


Figure 2. Excitation spectrum of $\text{Sr}_{2-x}\text{Si}_5\text{N}_8:\text{Eu}_x^{2+}$ ($x=0.02$) phosphors synthesized under 632 nm emission

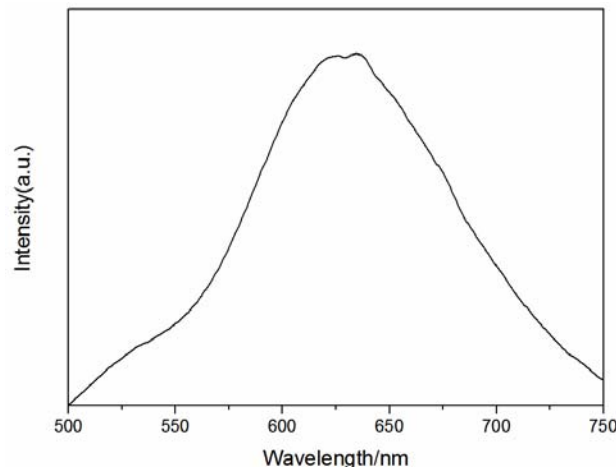


Figure 3. Emission spectrum of $\text{Sr}_{2-x}\text{Si}_5\text{N}_8:\text{Eu}_x^{2+}$ ($x=0.02$) phosphors synthesized under 426 nm excitation

Figure 2 shows the excitation spectrum of $\text{Sr}_{2-x}\text{Si}_5\text{N}_8:\text{Eu}_x^{2+}$ ($x=0.02$) phosphors synthesized under 632 nm emission. The broad excitation bands ranging from 360 nm to 500 nm were observed in the excitation spectrum and the wide absorption peaking ranging from 400 nm to 450 nm. The peaking centered at 426 nm is attributed to the direct excitation of Eu^{2+} ion via the $4f^7-4f^65d^1$ parity allowed transition [21].

Figure 3 shows the emission spectrum of $\text{Sr}_{2-x}\text{Si}_5\text{N}_8:\text{Eu}_x^{2+}$ ($x=0.02$) phosphors synthesized under 426 nm excitation. It is clear that the emission spectrum exhibits an intense broad band ranging from 500 to 750 nm peaking at 632 nm, which is attributed to the transition from the $4f^65d^1$ excited states to the $4f^7$ ground state of Eu^{2+} ion.

Upon irradiation at different wavelengths within the excitation spectrum, the emission spectrum put up similar emission of Eu^{2+} in peak shape and position, indicating the occurrence of energy transfer between the base material and the Eu^{2+} activators. Due to the high covalent environment around Eu^{2+} ion, emission of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphor was observed at a fairly longer wavelength region. This intense broad excitation band located at the near-UV and visible light spectral range provides the basis for developing this kind of phosphors for white light-emitting diodes (WLEDs) conversion applications [22].

3.3. Luminescence Decay Lifetime of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ Phosphors

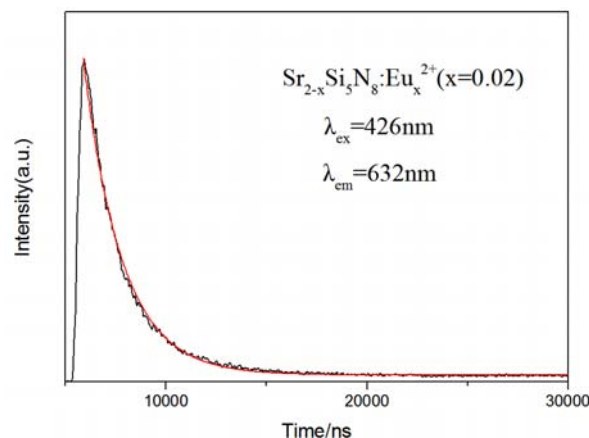


Figure 4. Luminescence decay curve of $\text{Sr}_{2-x}\text{Si}_5\text{N}_8:\text{Eu}_x^{2+}$ ($x=0.02$) phosphors ($\lambda_{\text{ex}}=426$ nm, $\lambda_{\text{em}}=632$ nm).

Figure 4 shows the luminescence decay curve of $\text{Sr}_{2-x}\text{Si}_5\text{N}_8:\text{Eu}_x^{2+}$ ($x=0.02$) phosphors monitored at $\lambda_{\text{ex}}=426\text{ nm}$, $\lambda_{\text{em}}=632\text{ nm}$. To reveal the lifetimes of as-prepared phosphors, computer-aided simulations of the experimental data were conducted, and the fitting result are also shown in Figure 4 as red curve.

The decay of the Eu^{2+} is non-exponential and is considered as superposition of two components. The decay curve of Eu^{2+} luminescence was fitted to two exponential decay given by the following equation:

$$I(t) = I_0 + A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (1)$$

Where τ_1 and τ_2 is the luminescence decay time, I_0 , A_1 and A_2 is the fitting parameters. The squares sum of error of fitting χ^2 is 1.79, shows to matching and achieved a good result. Finally, we can found the lifetime of Eu^{2+} in the $\text{Sr}_2\text{Si}_5\text{N}_8$ host is 1919.81 ns.

3.4. The CIE chromaticity coordinates of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ Phosphors

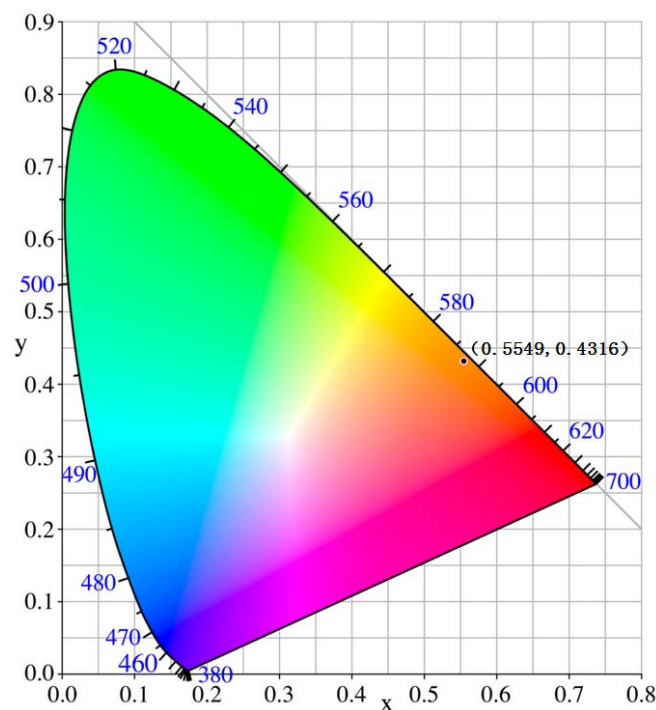


Figure 5. The CIE chromaticity coordinates of $\text{Sr}_{2-x}\text{Si}_5\text{N}_8:\text{Eu}_x^{2+}$ ($x=0.02$) phosphors ($\lambda_{\text{ex}}=426\text{ nm}$, $\lambda_{\text{em}}=632\text{ nm}$).

The red emission of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphors can be confirmed by the CIE (Commission International de L' Eclairage 1931 chromaticity) coordinates from their emission spectra. Figure 5 shows upon excitation by 426 nm, the CIE chromaticity coordinates of $\text{Sr}_{2-x}\text{Si}_5\text{N}_8:\text{Eu}_x^{2+}$ ($x=0.02$) phosphors are ($x=0.5549$, $y=0.4316$).

4. Conclusion

We have reported a simple synthetic route to $\text{Sr}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$ based red phosphors for white light-emitting diodes (WLEDs), through the chemical reaction of SrCO_3 , Si_3N_4 and Eu_2O_3 at 1600°C under N_2 atmosphere. The Eu^{2+} doped $\text{Sr}_2\text{Si}_5\text{N}_8$ nitride phosphors were synthesized by carbothermal reduction and nitridation method using carbon as main reduction agent, and NH_4Cl as a flux. $\text{Sr}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$ phosphors structure were investigated using X-ray diffraction (XRD). The XRD result indicate that the Eu^{2+} ions are effectively doped into the $\text{Sr}_2\text{Si}_5\text{N}_8$ host lattice. And the samples are indexed with an orthorhombic lattice with the space group of $\text{Pmn}2_1$. Excitation spectrum of $\text{Sr}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$ phosphors showed a broad excitation bands peaking at 632 nm by both UV and blue light. There is an asymmetric wide emission peaks between 500 nm and 750 nm originated from the $4f^65d^1-4f^7$ transitions of Eu^{2+} ion. And the lifetime of Eu^{2+} in the $\text{Sr}_2\text{Si}_5\text{N}_8$ host is 1919.81 ns. The CIE chromaticity coordinates of $\text{Sr}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$ phosphors are ($x=0.5549$, $y=0.4316$). The experimental spectroscopic results presented in this work show the $\text{Sr}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$ phosphors as an excellent candidate for getting red emission for White light-emitting diodes.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (NSFC) (Grant No. 21361028 and Grant No. 21661036).

References

- [1] C.H. Lu, P.C. Wu, Reaction mechanism and kinetic analysis of the formation of Sr_2SiO_4 via solid-state reaction, *J. Alloys Compd.* 466 (2008) 457.
- [2] S. Nakamura, T. Mukai, M. Senoh, Candela-class high-brightness $\text{InGaN}/\text{AlGaIn}$ double-heterostructure blue-light-emitting diodes, *Appl. Phys. Lett.* 64 (1994) 1687.
- [3] Y. Liang, D. Yu, W. Huang, M. Zhang, G. Li, C. Yan, Molten salt synthesis and luminescent properties of nearly spherical YAG:Ce phosphor, *Mater. Sci. Semicon. Proc.* 30 (2015) 92-97.
- [4] V. Bachmann, C. Ronda, A. Meijerink, Temperature quenching of yellow Ce^{3+} luminescence in YAG:Ce , *Chem. Mater.* 21 (2009) 2077-2084.
- [5] A. Aboulaich, M. Michalski, R. Schneider, A. Pot Devin, J. Deschamps, R. Deloncle, G. Chadeyron, R. Mahiou, Ce-doped YAG nan phosphor and red emitting $\text{CuInS}_2/\text{ZnS}$ core/shell quantum dots for warm white light-emitting diode with high color rendering index, *ACS Appl. Mater. Interfaces* 6 (2014) 252 - 258.
- [6] Z. Mao, Y. Zhu, Y. Wang, L. Gan, $\text{Ca}_2\text{SiO}_4\text{:Ln}$ ($\text{Ln}=\text{Ce}^{3+}$, Eu^{2+} , Sm^{3+}) tricolor emission phosphors and their application for near-UV white light-emitting diode, *J. Mater. Sci.* 49 (2014) 4439 - 4444.
- [7] R. Mueller-Mach, G. Mueller, M. R. Krames, H. A. Höpfe, F. Stadler, W. Schick, T. Jüstel and P. Schmidt, Highly efficient all-nitride phosphor-converted white light emitting diode. *Phys. Status Solidi A*, 2005, 202, 1727-1732.
- [8] P. Waltereit, O. Brandt, A. Trampert, H.T. Grahn, J. Menniger, M. Ram Steiner, M. Reiche and K.H. Ploog, Nitride semiconductors free of electrostatic fields for efficient white light-emitting diodes. *Nature*, 2000, 406, 865-868.
- [9] V.D. Luong, W.T. Zhang, H.R. Lee, Preparation of $\text{Sr}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$ for white light-emitting diodes by multi-step heat treatment, *J. Alloys Compd.* 509 (2011) 7525-7528.
- [10] X.Q. Piao, K. Machida, T. Hirakata, H. Hanzawa, Y. Shimomura, N. Kijima, Preparation of $\text{CaAlSiN}_3\text{:Eu}^{2+}$ phosphors by the self-propagating high-temperature synthesis and their luminescent properties, *Chem. Mater.* 19 (2007) 4592-4599.
- [11] O.M. ten Kate, Z. Zhang, P. Dorenbos, H.T. Hintzen, E. van der Kolk, 4f and 5d energy levels of the divalent and trivalent lanthanide ions in $\text{M}_2\text{Si}_5\text{N}_8$ ($\text{M}=\text{Ca}$, Sr , Ba), *J. Solid State Chem.* 197 (2013) 209-217.
- [12] Y.Q. Li, N. Hirosaki, R.J. Xie, T. Takeda, M. Mitomo, Yellow-orange-emitting $\text{CaAlSiN}_3\text{:Ce}^{3+}$

- phosphor: structure, photoluminescence, and application in white LEDs, *Chem. Mater.* 20 (2008) 6704 - 6714.
- [13] T. Wang, P. Zheng, X. Liu, H. Chen, L. Bian, Q.L. Liu, Effects of replacement of AlO^+ for SiN^+ on the structure and optical properties of $\text{Sr}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$ phosphors, *J. Lumin* 147 (2014) 173 - 178.
- [14] M. Zeuner, P.J. Schmidt, W. Schick, One-pot synthesis of single-source precursors for nan crystalline LED phosphors $\text{M}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$ ($\text{M}=\text{Sr}, \text{Ba}$), *Chem. Mater.* 21 (2009) 2467 - 2473.
- [15] A. Lazarowska, S. Mahlik, M. Grinberg, C.W. Yeh, R.S. Liu, Spectroscopic properties and energy level location of Eu^{2+} in $\text{Sr}_2\text{Si}_5\text{N}_8$ phosphor, *Opt. Mater.* 37 (2014) 734 - 739.
- [16] H.S. Kim, K. Machida, T. Hirakata, H. Hanzaw, Luminescence properties of $\text{CaAlSiN}_3\text{:Eu}^{2+}$ phosphor prepared by direct-nitriding method using fine metal hydride powders, *J. Alloys Compd.* 633 (2015) 97-103.
- [17] Y. Hu, W. Zhuang, H. He, R. Liu, G. Chen, Y. Liu, X. Huang, High temperature stability of Eu^{2+} -activated nitride red phosphors, *J. Rare Earth* 32 (2014) 12-16.
- [18] M. Zeuner, F. Hintze, W. Schick, Low temperature precursor route for highly efficient spherically shaped LED-phosphors $\text{M}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$ ($\text{M}=\text{Eu}, \text{Sr}, \text{Ba}$), *Chem. Mater.* 21 (2009) 336-342.
- [19] R.J. Xie, N. Hirosaki, T. Suehiro, F.F. Xu, and M. Mitomo, A simple, efficient synthetic route to $\text{Sr}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$ -based red phosphors for white light-emitting diodes, *Chem. Mater.* 18 (2006) 5578-5583.
- [20] S. Ye, F. Xiao, Y.X. Pan, Y.Y. Ma and Q.Y. Zhang, Phosphors in phosphor-converted white light-emitting diodes: Recent advances in materials, techniques and properties, *Mater. Sci. Eng, R*, 71 (2010) 1-34.
- [21] Y.Q. Li, C. M. Fang, G. de With, H.T. Hintzen, Preparation, structure and photoluminescence properties of Eu^{2+} and Ce^{3+} -doped SrYSi_4N_7 , *J. Solid State Chem.* 177 (2004) 4687-4694.
- [22] X. Piao, K. Machida, T. Hirakata, H. Hanzawa, Y. Shimomura, and N. Kijima, Preparation of $\text{CaAlSiN}_3\text{:Eu}^{2+}$ phosphors by the self-propagating high-temperature synthesis and their luminescent properties, *Chem. Mater.* 19 (2007) 4592 – 4599.