Role of pressure in stabilization of oxynitride phosphor synthesis

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Abstract

The possibilities of improving the crystallization and optical properties of strontium europium oxonitridosilicate phosphor powders were discussed. Two different routes of synthesis were presented: traditional solid-state reaction method and gas pressure synthesis. It was proven that altering the partial pressure during the process of synthesis enhances crystallization of a desired single, triclinic $\text{SrSi}_2\text{O}_2\text{N}_2$ phase. XANES measurements confirmed complete reduction of the trivalent europium activator ions in all of the tested materials. The photoluminescent properties were determined by emission, excitation and decay times measurements. CIE1931 colour points and luminous efficacy were calculated as well. Thermal quenching studies in the range of 0–225 °C confirmed good thermal stability of the investigated powders combined with excellent quantum efficiency at room temperature.

Keywords LED · Oxynitride phosphor · Photoluminescence · Synthesis · Solid state reaction · Extended X-ray absorption structure (EXAFS · XANES)

1 Introduction

Solid state lighting, as an alternative for incandescent and fluorescent lamps, has received increasing interest for many years, due to energy savings, long life and durability of the devices and great quality of the obtained light. The 2014 Nobel Prize for S. Nakamura, I. Akasaki and H. Amano for the invention of InGaN-based high brightness double-heterostructure blue LEDs stressed the significance of the research in the area of materials for white LEDs and the importance of white LEDs for society.

Nowadays, one of the most widely used activator ions for phosphors for white LED's excited by blue/UV radiation is Eu^{2+} due to its 4f–5d transition which ensures both wide emission and excitation bands, strongly depending on the local environment. In the last two years, publications on various hosts for Eu^{2+} ions were reported [1–7], shifting the emission maxima from blue to red. Despite this fact, the

well-known europium-doped $\text{SrSi}_2\text{O}_2\text{N}_2$ oxynitride phosphor still attracts significant attention, as one of the most suitable green phosphors for white LEDs, characterized by high quantum efficiency, chemical stability, high colour purity, limited thermal quenching and a broad excitation band [8–11]. However, it seems that further research on this compound is necessary, especially on the crystal structure and synthesis methods. A triclinic crystal structure of this compound isotypic to $\text{EuSi}_2\text{O}_2\text{N}_2$ was reported by Seibald et al. and Oeckler et al. [10, 12]. This oxynitride is characterized by a low symmetry layered structure, as a result of three-fold bridging N^{3-} ions [10]. The compound can crystallize in the monoclinic system also, as Seibald et al. reported before [13]. This is why any modification of chemical composition or change of synthesis method/ parameters can bring many difficulties.

The $\text{SrSi}_2\text{O}_2\text{N}_2$ phosphor is usually obtained via a traditional, one-step solid-state reaction method presented in many publications [14–18] or via a two-step method [19, 20] including preparation of a strontium silicate precursor. Various Eu^{2+} concentrations and different synthesis parameters complicate the comparison of presented results. Nonetheless, comparing phosphors doped with 2 mol% of activator ions obtained at 1400 °C [8], 1450 °C [14] and 1500 °C [21] via the one-step method reveals that despite relatively

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small changes of synthesis parameters, diffuse reflection spectra can exhibit 1 or 2 minima, suggesting different absorption of the host lattice. The excitation and emission spectra are changing as well, especially the range and shape of excitation and FWHM of emission spectra. Another synthesis approach is a two-step solid-state reaction method, which is supposed to provide a greater control over ongoing reactions during synthesis. Zhang et al. [22] obtained $\text{Sr}_{0.98}\text{Eu}_{0.02}\text{Si}_2\text{O}_2\text{N}_2$ phosphor by synthesis of $\text{Sr}_2\text{SiO}_2\text{:Eu}^{3+}$ precursor with Si_3N_4 at 1450 °C. As the authors presented, a single triclinic oxynitride phase was obtained when a 1.1–1.5 ratio of $\text{Si}_3\text{N}_4/\text{Sr}_2\text{SiO}_4$ was used. In the materials discussed above [8, 21] next to the P1 space group structure, an additional unknown phase was visible in XRD patterns. Fang et al. [23], who conducted the same type of synthesis, proved that $\text{Sr}_{0.98}\text{Eu}_{0.02}\text{Si}_2\text{O}_2\text{N}_2$ phosphor obtained via a two-step synthesis was characterized by enhanced emission intensity and higher thermal stability in comparison to material obtained from a one-step process.

From these various results, it is clear that it is necessary to find better and more reproducible synthesis methods and conditions for these oxynitrides. One of the main drawbacks of the solid-state reaction method in a powder bed is the necessity of applying a flow of reducing/forming gas (nitrogen/hydrogen) during synthesis. This crucial factor enhances reduction of europium ions into a desired Eu^{2+} oxidation state and it controls the nitrogen partial pressure throughout the synthesis of oxynitride. Accordingly, a gas flow over the powder bed constantly removes gaseous reaction products. Thus, it results in a simultaneous change of the partial pressure of involved reactive gases what makes the solid-state method an even more unstable process. This is why a high gas pressure synthesis in a closed reactor appears as a promising replacement for conventional methods of obtaining oxynitride phosphors.

In the present study, $\text{Sr}_{0.96}\text{Eu}_{0.04}\text{Si}_2\text{O}_2\text{N}_2$ materials synthesized by 2 pathways are compared: via a traditional one-step solid-state reaction method in N_2/CO flow and via gas pressure synthesis at 6 MPa. Application of a high gas pressure during synthesis can improve not only the stability of the process, but also prevents evaporation of $\text{Si}_{(\text{g})}/\text{SiO}_{(\text{g})}$, resulting in a stoichiometry of the final powders much closer to the designed one. The influence of these factors on structural and optical properties of oxynitride phosphors is, certainly, not without significance. Following the work of McMillan [24], high pressure during synthesis can influence coordination numbers, valence states and therefore also optical properties such as increased absorption of material. To the best of our knowledge, there is no available research on the influence of such high gas pressure on the crystallization and optical properties of oxynitride phosphors. In addition, X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) were performed in

order to describe the local environment of activator ions and their oxidation state in the oxynitride structure, to clear the role of the essential factors to obtain pure green emission.

2 Materials and methods

$\text{Sr}_{0.96}\text{Eu}_{0.04}\text{Si}_2\text{O}_2\text{N}_2$ phosphors were obtained with raw materials SrCO_3 (Alfa Aesar, 99%), Eu_2O_3 (Treibacher, 99.99%), Si_3N_4 (Sigma Aldrich, 98%) and SiO_2 (Merck 99%). The molar fraction of silicon in SiO_2 in comparison with Si_3N_4 was slightly lower (0.2/1.8) than the stoichiometric one (0.5/1.5) in order to compensate oxygen contamination in the used silicon nitride powder. All investigated samples were homogenized via high energy ball milling (Fritsch Pulverisette 7; 500 rpm; 1 h; B/P ratio 4:1). In all cases, a one-step synthesis was applied. The sample obtained via the solid-state reaction (SSR) method was synthesized in N_2 (99.99%) flow in a graphite furnace (Thermal Technology) at 1450 °C during 4 h. A N_2 flow was applied throughout the process; thus gaseous products of the reaction were removed. Since the phosphor was synthesised via traditional way it will be concerned as a reference material for presented studies. Material prepared by gas pressure synthesis (GPS) was obtained in a graphite furnace (HIP AIP8-30H-PED, American Isostatic Presses) under a nitrogen pressure of 6 MPa in a closed reactor, at 1600 °C during 2 h. In this method, the $\text{CO}_{(\text{g})}$, formed as a result of carbonates decomposition, was not removed during synthesis. Powder X-ray diffraction (XRD) patterns were measured with 1°/min rate and 0.02° step on a Siemens D5000 diffractometer (40 kV, 40 mA) using $\text{Cu K}\alpha 1$ radiation ($\lambda = 0.154$ nm). The morphology and microstructure were observed in a scanning electron microscope (SEM; Hitachi S-3400 N) operating at 20 kV. Particle size distribution (PSD) measurements were performed on a Malvern Mastersizer3000 analyzer after 1 min. of ultrasonic treatment, assuming a refraction index $n = 1.75$. Reflection spectra were recorded using a Varian Cary 500 UV–Vis spectrometer equipped with an integrating sphere, in the 250–800 nm range. BaSO_4 powder was used as a reference. Emission and excitation spectra were recorded with an Edinburgh Instruments FS920 spectrometer, using a 450 W Xe arc lamp as the excitation source. Emitting colour, CIE 1931 chromaticity as well as luminous efficacy of investigated powders were calculated using the LED ColorCalculator software by Osram Sylvania [25]. Quantum efficiency (QE) measurements were performed using an integrating sphere coupled to an EMCCD camera (Princeton Instruments ProEM 16,002), attached to a spectrograph (Princeton Instruments Acton SP2358), using Al_2O_3 powder as a reference. Thermal quenching (TQ) measurements in the range 0–225 °C were performed using the same detection system.

In order to study the oxidation state and local environment of Eu activator ions in the crystal structure, X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption spectroscopy (EXAFS) measurements were performed. These measurements were carried out at the Dutch Belgian beam line (DUBBLE, BM26A) of the 6 GeV European Synchrotron Radiation Facility (ESRF) in Grenoble, France, operating with a 160–200-mA electron current [26]. The synchrotron radiation was monochromated with a double Si(111) monochromator, suppressing the higher harmonics. EuS and Eu₂O₃ were used as energy reference materials. Eu L_{III}-edge XANES and EXAFS spectra were recorded with an energy step of typically 1 eV. Spectra for the reference materials were collected in transmission mode using ion chambers. The XANES and EXAFS spectra of the phosphor powders were collected in fluorescence mode by monitoring the Eu Lα1 peak fluorescence line (centred around 5.85 keV). The phosphors could not be measured in

transmission mode because of the low dopant concentration and the relatively strong X-ray absorption of the host matrix. The X-ray fluorescence yield was detected with a nine element monolithic Ge detector [27]. Determination of the edge position, background subtraction, and normalization of the calibrated raw X-ray absorption data was performed using Athena [28].

3 Results

Figure 1 presents a comparison of the XRD patterns of the synthesized materials. It can be seen that the SSR material diffraction peaks, as well as those of the sample obtained by the GPS method, are consistent with the pattern of the SrSi₂O₂N₂ triclinic phase (ICDD# 01-076-3141). The relative intensities of some diffraction peaks are lower (e.g. 010; 110 or -110) or higher (e.g. 022 and 0-22 or 042 and

Fig. 1 XRD patterns of Sr_{0.96}Eu_{0.04}Si₂O₂N₂ phosphor obtained by solid-state reaction (SSR) and gas pressure synthesis (GPS): **a** full range of diagrams; **b** 24–40° 2θ range

Table 1 Comparison of FWHM values of the two strongest XRD peaks

Sample #	FWHM (2θ)	
	(020) $\sim 25.4^\circ$	(220);($\bar{2}10$) $\sim 31.5^\circ$
SSR	0.14	0.19
GPS	0.21	0.21

Fig. 2 SEM photographs and particle size distribution of studied materials

0–42) if compared to the standard pattern of triclinic polymorph. The intensity variation could be ascribed to several real crystal structure imperfections as twinning. Formation of twin domains which involves overlapping reflections in this polymorph was reported earlier [12, 20, 29]. Interestingly there are subtle differences in the phase composition between both compared samples, since additional peaks at 30.5° ; 31.2° ; 36.5° ; 37° ; 51.3° ; 56° and diffuse scattering are visible in the SSR specimen though noteworthy broadening of the peaks has been observed in the GPS one (Table 1). Observed deviations of diffraction patterns in a reference sample could originate from the stacking disorder and/or intergrowth in this layered triclinic oxonitridosilicate since they causes significant alterations in the X-ray diffraction pattern, concerning both line positions and widths. The mentioned deviations are slightly higher in the reference sample than in the GPS one. In summary of the XRD studies, it seems that applying GPS method led to manufacturing the monophase triclinic $\text{SrSi}_2\text{O}_2\text{N}_2\text{:Eu}^{2+}$ powder, as the SSR specimen was contaminated by an additional phase (marked in the diagram by the star).

SEM images and PSD graphs are presented in Fig. 2. The SSR sample is characterized by flakey particles with an average particle size of approx. $8\ \mu\text{m}$. Powders obtained via high pressure synthesis are characterized by flakey particles also; however, they are assembled into larger agglomerates with

diameter up to $60\ \mu\text{m}$. The reason of the enhanced particles growth is the intensified matter transport via diffusion during synthesis, as a result of 60 times higher nitrogen pressure and subsequent enhanced sintering.

The application of two synthesis methods: solid-state reaction or gas pressure synthesis led to formation of different final $\text{SrSi}_2\text{O}_2\text{N}_2\text{:Eu}^{2+}$ phosphor powders. Their diversity is visible in the phase composition, crystallite and particle size and resultant luminescence properties. First of all, solid-state synthesis with a significant amount of a covalent powder of $\alpha\text{-Si}_3\text{N}_4$ is a complex process related to the low coefficient of diffusion and high equilibrium partial pressure of $\text{Si}_{(\text{g})}/\text{SiO}_{(\text{g})}$ as a result of Si_3N_4 decomposition at elevated temperature in reducing atmosphere of a graphite furnace. Application of nitrogen high pressure prevents decomposition of Si_3N_4 and losses of volatiles in the final product; thus the monophase triclinic $\text{SrSi}_2\text{O}_2\text{N}_2$ could be obtained as it happened in the GPS sample. At the same time, nitrogen high pressure limited the crystal growth of the triclinic phase since broadening of XRD peaks was considerable, but it enhanced sintering of phosphor particles as the distribution of particles sizes shows (Fig. 2). The latter process could be explained by the rules of the first stage of sintering/densification. The pressure-assisted sintering occurs via particles sliding and rearrangement, while grain growth of the new phase is facilitated by atomic diffusion and/or by evaporation and condensation processes. It seems that both liquid-free syntheses, i.e. GPS and SSR, channel to the similar distorted crystal structure of the triclinic polymorph. The presence of the unknown phase in the SSR sample could be assigned to some material losses and the consequent deviation of $\text{SrSi}_2\text{O}_2\text{N}_2$ stoichiometry in both cations and anions ratio. Moreover, low FWHM values of the relevant diffraction peaks (Table 1) correspond to larger crystallites in SSR samples; thus nucleation of triclinic phase was somehow restricted.

Table 2 presents a summary of the measured optical properties. The reference sample is characterized by strong absorption in the blue range with maximum at $417\ \text{nm}$, which could be ascribed to $4f^7 \rightarrow 4f^65d^1$ transition in Eu^{2+} ions. Synthesis via the GPS method leads to a shift of the maximum absorption toward longer wavelengths. It was also possible to notice a difference in the absorption range from 250 to $300\ \text{nm}$ (not shown here) attributed to the absorption of the host [8]. The latter is related to the electron excitation from valence to conduction band and it could be affected by the details of the host crystal structure.

The sample obtained via gas pressure synthesis showed emission spectra (Fig. 3) characteristic for Eu^{2+} ions in a $\text{SrSi}_2\text{O}_2\text{N}_2$ crystal lattice—a single emission peak with maximum position at $\lambda_{\text{em}} = 535\ \text{nm}$, which can be ascribed to the $4f^65d^1 \rightarrow 4f^7$ transition in Eu^{2+} ions, corresponding to saturated green emission. It is good to point out that the

Table 2 Optical properties of materials obtained via different synthesis methods

Sample #	SSR	GPS
Body colour	Orange	Dark green
Max. absorption (nm)	418	431
Excitation range (nm)	240–506	234–510
Excitation max (nm)	370	370
Emission max (nm)	536	535
iQE (%)	62	61
eQE (%)	54	61
Luminous efficacy (lm/W)	486	520
Decay time, τ_1 (μ s)	0.401	0.594
Decay time, τ_2 (μ s)	1.006	1.1

Fig. 3 PL and PLE spectra of phosphors obtained via SSR or GPS method

emission spectrum of the SSR sample consists of an additional band, located at ~620 nm, which strongly affects the colour coordinates and decreases the colour purity (Fig. 4). Earlier works on $\text{SrSi}_2\text{O}_2\text{N}_2:0.02\text{Eu}^{2+}$ phosphors obtained via the solid-state reaction method reported also broadening of emission spectra in the form of an additional shoulder in the range of 400–500 nm (Song et al. [8]) or on the red side. Bachman et al. [30] explained a pronounced shoulder on the low energy side of the spectrum as originating from traces of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$. According to Liu et al. [31], emission spectra of this oxygen free phase cover the 540–800 nm range with maximum position at 625 nm, when the material is synthesized at 1450 °C. In this cited paper, the additional nitride phase was not recognized in XRD patterns; however, the lower sensitivity of this method has to be taken into account. According to Liu et al., both $\text{SrSi}_2\text{O}_2\text{N}_2$ and $\text{Sr}_2\text{Si}_5\text{N}_8$ phases crystallize at the same temperature – 1200 °C; however, the $\text{Sr}_2\text{Si}_5\text{N}_8$ phase could be detected by XRD only if a higher synthesis temperature was applied.

Fitting the emission spectra of the reference specimen with the symmetric Gaussian line shape were performed

Fig. 4 CIE1931 colour coordinates at room temperature (fully filled markers) and at 225 °C (half full markers) of phosphors obtained via SSR or GPS method

for emission spectrum converted to energy scale. A second emission maximum at about 576 nm was revealed, which is too low to be ascribed to the $\text{Sr}_2\text{Si}_5\text{N}_8$ phase but close to $\text{Sr}_3\text{SiO}_5:\text{Eu}^{2+}$ with reported emission maximum at 566 nm under 395 nm excitation [32]. Presence of this strontium-rich silicate could imply some Si losses before $\text{SrSi}_2\text{O}_2\text{N}_2$ synthesis started.

As mentioned above, solid-state synthesis of $\text{SrSi}_2\text{O}_2\text{N}_2$ carried out in reducing atmosphere with simultaneous gas flow increases the probability of silica reduction. For this reason, features like synthesis temperature, reduction atmosphere and silicon mono-oxide partial pressure ($\text{SiO}_{(g)}$) should be considered. During the solid-state reaction, both silica sources (Si_3N_4 and SiO_2) are continuously reduced in CO atmosphere at high temperature according to reaction (1)

However, the side reaction could also occur at higher temperature:

Reaction (2) is controlled by partial pressure of the reactive gases: $\text{SiO}_{(g)}$, $\text{CO}_{(g)}$, $\text{N}_{2(g)}$ accomplishment of ($\text{SiO}_{(g)}$) partial pressure equilibrium point at given temperature would terminate the decomposition of solids, however applying the continuous gas flow makes it more complex. It clearly shows that oxygen and/or nitrogen losses from solids could be observed as well. Consequently, the presence of strontium and oxygen richer Sr_3SiO_5 is possible.

In case of gas pressure synthesis conducted in a closed reactor chamber, the reducing atmosphere is obtained by SrCO_3 decomposition, leading to CO/CO_2 presence. What follows, partial pressure of $\text{CO}_{(g)}$ and $\text{SiO}_{(g)}$ depends only

on applied nitrogen pressure. As a result, the high partial pressure of nitrogen moves reaction (2) to the left side which limits an amount of silicon monoxide volatilization. This is why application of high pressure during synthesis resulted in elimination of the red part of the spectra in comparison with the sample obtained by solid-state reaction. Based on the presented considerations, we could conclude that higher phase purity with designed stoichiometry of this phosphor has been accomplished during gas pressure synthesis.

External (eQE) and internal (iQE) quantum efficiency (Table 2) of the SSR sample is approx. 55 and 60%, respectively. The external quantum efficiency is lower, since then, not all of the incident photons are taken into account. Gas pressure synthesis leads to equalization of iQE and eQE values, corresponding to an almost 100% absorption of the incident light. The dark green colour of the GPS powder might suggest lower quantum efficiency in comparison with the bright SSR material. On the contrary, the eQE is higher, presumably due to an increased absorption efficiency of the powders obtained in high pressure environment. Lower than expected quantum efficiency of GPS specimens could be ascribed to residual carbon precipitates (dark green colour) because of high partial pressure of CO in the closed reactor. One notes very high quantum yield of $\text{SrSi}_2\text{O}_2\text{N}_2\text{:Eu}^{2+}$ reported lately for the phosphor manufactured directly from SrO without carbon oxides presence [33]. Luminous efficacy, calculated from obtained emission spectra, is higher for GPS sample as well (520 lm/W), due to pure green colour of the sample. Lower luminous efficacy determined for the SSR sample (486 lm/W) was a results of a ‘tail’ in the emission spectrum in the deep red, where the eye sensitivity is low (see Fig. 3).

Thermal quenching of investigated samples (Fig. 5) performed in 0–225 °C range confirmed that emission intensity of the samples is reduced less than 50% at 225°. The SSR was expected to have lower thermal stability in comparison with the second sample, due to phase impurity issues causing internal stresses of crystal lattice and increased amount of defects. Indeed, higher temperature stability was observed in sample obtained via gas pressure synthesis method. The emission intensity decreased by only 39% at 225 °C for this sample, which is an excellent value in view of possible application as LED phosphor, where LED chip temperatures typically rise up to 150 °C. Despite the fact that the sample obtained via GPS is thermally more stable than SSR material (43% decrease of intensity), the results are quite similar. For both materials, there is no significant change of the colour point at high temperatures (Fig. 4). The slight change of thermal quenching in both tested specimens occurs at about 100 °C and could be ascribed to $\text{Sr}_3\text{SiO}_5\text{:Eu}$ presence in SSR phosphor since the abrupt decrease in Eu^{2+} emission intensity over 100 °C was reported earlier [34].

Fig. 5 Temperature dependence of PL intensity of materials obtained via SSR and GPS

The shape of the fluorescent decay curves of the GPS obtained specimen indicates a bi-exponential behaviour, as expected from the relatively high amount of activator ions.

(4 mol%). Calculated values of both decay components are presented in Table 2. Sample obtained by GPS shows lifetimes of approx. 0.6 μs for the first exponential and approx. 1.1 μs for the second exponential, higher than that of the SSR phosphor, and corresponding with a lower non-radiative decay rate. All presented results show that applying high pressure in a synthesis is the optimum way to obtain highly efficient green oxynitride phosphor powders.

Proper reduction of the oxidation state of the activator ions is one of the crucial factors to obtain desirable optical properties of Eu-doped phosphors, as shown by Xie et al. [35]. XANES measurements were performed for both studied phosphors. It is good to point out that almost complete reduction of Eu^{3+} ions was achieved (Fig. 6) for the materials, which is quite unusual for oxynitride phosphors in general, making broadening the knowledge on synthesis methods/parameters even more desirable. The results show that the 2+ oxidation state of Eu was obtained using both synthesis methods and the high amount of Eu^{2+} could be related rather to the synthesis in a reducing atmosphere of CO/N_2 rather than to gas pressure. Despite similar results obtained for both studied materials, the GPS sample exhibits the most efficient reduction of Eu^{3+} ions. Those results are consistent with higher eQE and improved thermal stability in comparison to the SSR material.

Incorporation of the Eu ions in host lattice was studied as well using EXAFS. The Eu ion is able to build in 8 different Sr sites [12] which are coordinated by 6 O atoms and 1 N atom, with a preferential substitution on the standard sites (Sr1, Sr2, Sr3 and Sr4). A detailed EXAFS

Fig. 6 XANES spectra of reference materials EuS (for the Eu^{2+} oxidation state), Eu_2O_3 (for the Eu^{3+} oxidation state) and samples coming from solid-state reaction (SSR) and gas pressure synthesis (GPS)

analysis (not shown) was performed using multiple data sets fitting on all three samples. For all spectra, a Hanning window was used (k -range: $2.4 \text{ \AA}^{-1}$, $7.9 \text{ \AA}^{-1}$], and R -range: $[1 \text{ \AA}, 4.3 \text{ \AA}]$). The triclinic crystal structure of $\text{SrSi}_2\text{O}_2\text{N}_2$ was used to generate the scattering paths for X-rays being absorbed by Eu ions on the standard Sr sites of the lattice. This analysis showed that the investigated samples are characterized by preferential occupation of the Sr2 site (approximately 60% of the Eu ions). The rest of the Eu ions occupy the Sr4 site in the crystal matrix. This effect can be explained by the similar distances ($\text{Eu}-\text{O}$) in the Sr2 ($2.5889 \text{ \AA}$) and Sr4 sites ($2.6709 \text{ \AA}$), compared to the ($\text{Eu}-\text{O}$) distance in EuO ($2.5710 \text{ \AA}$) according to PDF database patterns (# 00-015-0886; #00-006-0520). This distribution of Eu^{2+} ions over two separate Sr sites is compatible with the occurrence of bi-exponential decay curves as presented above.

4 Conclusions

In this work, $\text{Sr}_{0.96}\text{Eu}_{0.04}\text{Si}_2\text{O}_2\text{N}_2$ phosphors were successfully synthesized via the one-step gas pressure or solid-state synthesis. All studied oxynitride phosphors are characterized by the triclinic $\text{SrSi}_2\text{O}_2\text{N}_2$ phase and show emission band with maximum at 536 nm. XANES measurement confirmed for the first time, complete reduction of the trivalent activator ions in all of the materials. In addition, it has been shown using EXAFS that Eu^{2+} ions occupy two sites in crystal lattice—Sr2 and Sr4 site. Never reported before, this direct comparison of phosphors obtained by solid-state reaction and gas pressure synthesis methods enables to deduce the following:

- It has been proven that applying high pressure during the synthesis was effective in formation of triclinic $\text{SrSi}_2\text{O}_2\text{N}_2$ phase powder phosphor and elimination of phase contamination, what proves that applying high pressure during synthesis provides better control over Si:Sr and O:N ratio as well as reduction of activator ions, opening possibilities for more reproducible optical properties. Due to the more efficient reduction of the europium activator to Eu^{2+} and improved crystallization of the oxynitrides phase, the material is characterized by enhanced optical properties in comparison with material resulting from the traditional solid-state reaction method.
- The material from gas pressure synthesis is characterized by the most efficient reduction of activator ions. This results in the best thermal stability and luminous efficacy among studied materials, suggesting a more rigid crystal lattice of materials obtained via gas pressure synthesis method.

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Data availability The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Declarations

Conflict of interest The authors have no conflict of interest to declare that are relevant to the content of this article.

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