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Structure and Photoluminescence Properties of $EuSiN_2$

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With the europium nitridosilicate, $EuSiN_2$ a novel member of the multifaceted MSiN$_2$ family is presented and compared with the structural similar compounds MSiN$_2$ (M = Ca, Sr, Ba). A different way of presenting the structure as M-N polyhedra layers is introduced. The crystal structure of $EuSiN_2$, being isotypical to $SrSiN_2$, was determined and refined based on powder X-ray diffraction data in space group $P2_1/c$ (no. 14) with a = 5.96381(2) Å, b = 7.25982(3) Å, c = 5.488338(19) Å, β = 113.33°, V = 218.18(5) Å^3, and Z = 4. As the Eu^{2+}-doped MSiN$_2$ compounds show excellent luminescence properties as LED phosphors, the luminescence behaviour of dark red emitting $EuSiN_2$ has been investigated as well. Two emission peaks are visible at 708 nm and 764 nm. Many europium-doped nitridosilicates show more or less developed shoulders for their luminescence peaks, but two clearly shaped emission peaks are a novel feature for nitridosilicates. Comprehensive and detailed comparisons are given and discussed based on works in literature.
The chromaticity coordinate positions of $EuSiN_2$ in the CIE 1931 diagram are $x = 0.678$ and $y = 0.284$.

1. Introduction

Rare-earth activated nitridosilicate phosphors are attractive materials for phosphor-converted white light-emitting diodes (pc-LEDs), because of their auspicious chemical and physical properties.[1,2] Their wide-ranging applicability can be ascribed to their significantly extended structural varieties built on covalent SiN_4 network structures providing possible migration pathways[3–5] for cation exchange and their excellent thermal, chemical, and mechanical stability. An extensive series of MSiN$_2$ compounds (M = Be, Mg, Ca, Sr, Ba, Zn)[6–18] is already known in literature, standing out due to their multifaceted application in industry as, e.g., sinter additives for Si_3N_4 high performance ceramics[19–21] or Eu^{2+}-doped LED phosphors, showing excellent luminescence properties with a typical broadband emission for Eu^{2+} in the orange-red region.[20,22–33] The luminescence properties of Eu^{2+}-doped MSiN$_2$ (M = Mg, Ca, Sr, Ba) are influenced by the crystal structure of the host lattice, the degree of covalency, the crystal field environment, the size of the cation, the crystallographic M site, and the coordination of its next neighbours. The increase of the Eu^{2+} concentration causes a red-shift of the emission peaks of MSiN$_2$ (M = Sr, Ba). However, a fine tuning of the luminescence properties can be influenced by the respective Sr/Ba-ratio (at fixed Eu^{2+} concentration).[29,30]

Beyond the luminescent aspect, polymeric nonmetallic nitrides are considered as well as very important materials in the development of high-performance devices for optoelectronic applications. Crucial here are bulk electronic properties such as band gaps, high thermal conductivity, and low electrical conductivity, and in this context the M-Si-N compounds (M = Mg, Ca, Sr, Ba, Zn) have been studied comprehensively.[7,11]

The combination of nitridosilicate anionic host structures with M^{2+} and M^{3+} cations was an unknown phenomenon till Huppertz *et al.*[34] reported on the first nitridosilicate ($EuYbSi_4N_7$), comprising Eu^{2+} and Yb^{3+} cations. A few years later Hintzen *et al.*[35] published the isostructural compound $EuYSi_4N_7$. Eu_2SiN_3,[36] a mixed valenced (Eu^{2+} and Eu^{3+}) nitridosilicate, is a chain-type silicate comprising 1D infinite nonbranched *zweier* chains of corner-sharing SiN_4-tetrahedra. There are two crystallographically distinct europium sites at two different Wyckoff positions being occupied with Eu^{2+} and Eu^{3+}, respectively.

$M_2Si_5N_8$:Eu^{2+} (red-orange, 2-5-8 phosphors) and MSi$_2$O$_2$N$_2$:Eu^{2+} (yellow-green,1-2-2-2 phosphors) (M = Ca, Sr, Ba) were significant discoveries in the field of Eu-doped phosphors.[33,37–50]

Also $Eu_2Si_5N_8$ has been discovered long before and was already subject of multiple investigations, as, e.g., magnetic susceptibility measurements, DFT, and optoelectronic investigations,[34,51–53] however no detailed luminescence studies can be found in literature except the luminescence spectra of $Eu_2Si_5N_8$ Huppertz showed in his dissertation.[53]

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Table 1. Crystallographic data for $EuSiN_2$, (standard deviation in parentheses).

Formula	$EuSiN_2$
Formula mass / g mol^{-1}	208.06
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
Cell parameters / Å	$a = 5.96381(2)$
	$b = 7.25982(3)$
	$c = 5.488338(19)$
	$\beta = 113.33°$
Cell volume / $Å^3$	218.18(5)
Formula units / cell	4
Diffractometer	STOE STADI P
Radiation / Å	Co-$K\alpha_1$ ($\lambda = 1.788965$ Å)
Monochromator	Ge 111 (curved)
Temperature / K	293
Data range (2θ), step width	$4° \leq 2\theta \leq 85°$, 0.01°
Structure refinement	Rietveld refinement, Fullprof[54]
Background treatment	25 fixed background points
Profile function	Pseudo-Voigt (no. 7)
R_{Bragg}	3.06
R_{value}	1.95
GoF	1.2
Reduced χ^2	1.39

Herein, we present a novel europium nitridosilicate, namely $EuSiN_2$, together with its luminescence properties and a detailed structure comparison with the related compounds $MSiN_2$ (M = Ca, Sr, Ba).

2. Results

2.1. Synthesis and Structure Characterization

$EuSiN_2$ was synthesized from EuN and β-Si_3N_4 (Chempur 99.999%), according to the reaction in Equation (1). Hereby, a dark red powder was obtained. For detailed information see experimental part.

$$3\,EuN + Si_3N_4 \xrightarrow[1550\,°C]{N_2} 3\,EuSiN_2 + \frac{1}{2}N_2 \qquad (1)$$

The crystal structure of $EuSiN_2$ was determined and refined based on X-ray powder diffraction data in space group $P2_1/c$ (no. 14) with $a = 5.96381(2)$ Å, $b = 7.25982(3)$ Å, $c = 5.488338(19)$ Å, $\beta = 113.33°$, $V = 218.18(5)$ $Å^3$, and $Z = 4$.

The X-ray measurements were performed on a STOE STADI P powder diffractometer (see Table 1 and experimental part). The sample, which was slightly air sensitive, was enclosed and protected against atmosphere in a glass capillary with 0.3 mm diameter. Figure 1 shows the observed and calculated X-ray powder diffraction pattern as well as their difference curve after Rietveld refinement.[54] Crystallographic data and details of the Rietveld refinement are listed in Table 1. The occupied Wyckoff sites and refined atomic coordinates of $EuSiN_2$ are displayed in Table 2. For selected bond lengths of $EuSiN_2$ see Table 3. Estimated standard deviations are calculated in agreement with *ref.*[55]

Table 2. Occupied Wyckoff sites, refined atomic coordinates (Å) of $EuSiN_2$. (estimated standard deviations in parentheses).

Compound	Atom	Wyck.	x	Y	z	Occ.	U_{iso}
$EuSiN_2$	**Eu1**	*4e*	0.34083(13)	0.57128(7)	0.17583(15)	1	0.0144(2)
	Si1	*4e*	0.1088(4)	0.1458(2)	0.0653(5)	1	0.0144(2)
	N1	*4e*	0.2303(7)	0.5917(7)	0.5962(9)	1	0.0144(2)
	N2	*4e*	0.2172(7)	0.2353(6)	0.3801(11)	1	0.0144(2)

Table 3. Selected bond lengths (Å) of $EuSiN_2$. (standard deviations in parentheses).

Atom	Distance	Atom	Distance
Eu1-N1	2.643(5)	Eu1-N1	2.528(5)
Eu1-N1	2.642(4)	Eu1-N2	2.682(4)
Eu1-N1	2.901(5)	Eu1-N2	3.018(5)
Eu1-N1	2.988(5)	Eu1-N2	3.127(4)
Si1-N1	1.853(5)	Si1-N2	1.649(6)
Si1-N1	1.901(4)	Si1-N2	1.716(6)

$EuSiN_2$, being isotypical to $SrSiN_2$, crystallizes in space group $P2_1/c$ and is built up by a 2D highly condensed nitridosilicate framework with vertex-and edge-sharing SiN_4-tetrahedra (see Figure 2a). The structure consists of pairs of edge-sharing SiN_4-tetrahedra to form bow-tie-shaped Si_2N_6 dimers, which share vertexes to form layers (see Figure 3a and 4a).

In $EuSiN_2$ these SiN_4-tetrahedra layers were separated by cations (see Figure 3a), whereas taking other alkaline-earth elements into account, cation size plays a dominant role for the structure formation. [10,29]

This structure motif can be found for $MSiN_2$ (M = Sr, Ba)[10,29] as well (Figure 3b and d), while $CaSiN_2$ has a SiN_4-tetrahedra network structure. (see Figure 2c and 3c) But it has to be mentioned that Sr- and $BaSiN_2$[10,29] are not isotypical, what becomes clear having a look at Figure 2b and d and Figure 4b and c. In $EuSiN_2$, having only one crystallographic M cation site, an eightfold nitrogen coordination is observed as it can be found in $MSiN_2$ (M = Sr, Ba)[10,29] as well (see Figure 4d).

In $CaSiN_2$,[10,29] being isotypical to $KGaO_2$[56] as well as HP-$CaSiN_2$,[13] these SiN_4-tetrahedra build condensed *Sechser*-rings[57] with two different formations (see Figure 2c). For $EuSiN_2$ and $SrSiN_2$ the triangle formations have disappeared and only distorted *Sechser*-rings[57] remain (see Figure 2a and b). The end member $BaSiN_2$, however, displays with 119° nearly perfectly shaped *Sechser*-rings[57] (see Figure 2d). So it becomes clear that the cation size plays a very important role for the crystal structure as was already shown for other nitridosilicates.[58]

$SrSiN_2$[10,29] crystallizes in the same space group as $EuSiN_2$ ($P2_1/c$) to which it is isotypical and has only very slight differences

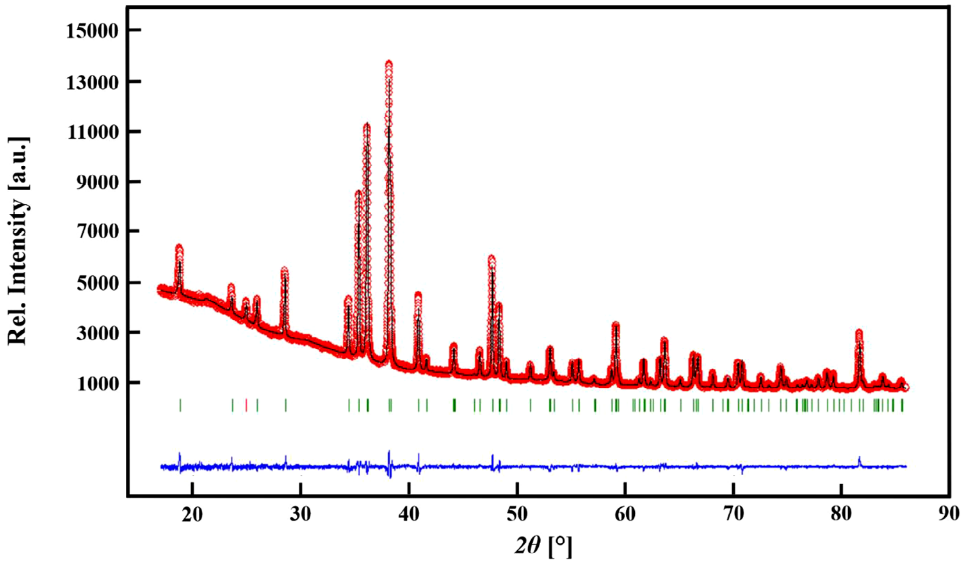

Figure 1. Observed (black) and calculated (red) X-ray powder diffraction pattern of $EuSiN_2$ as well as the position of Bragg reflections (green bars) together with their difference curve (blue) after Rietveld refinement (λ = 1.788965 Å).

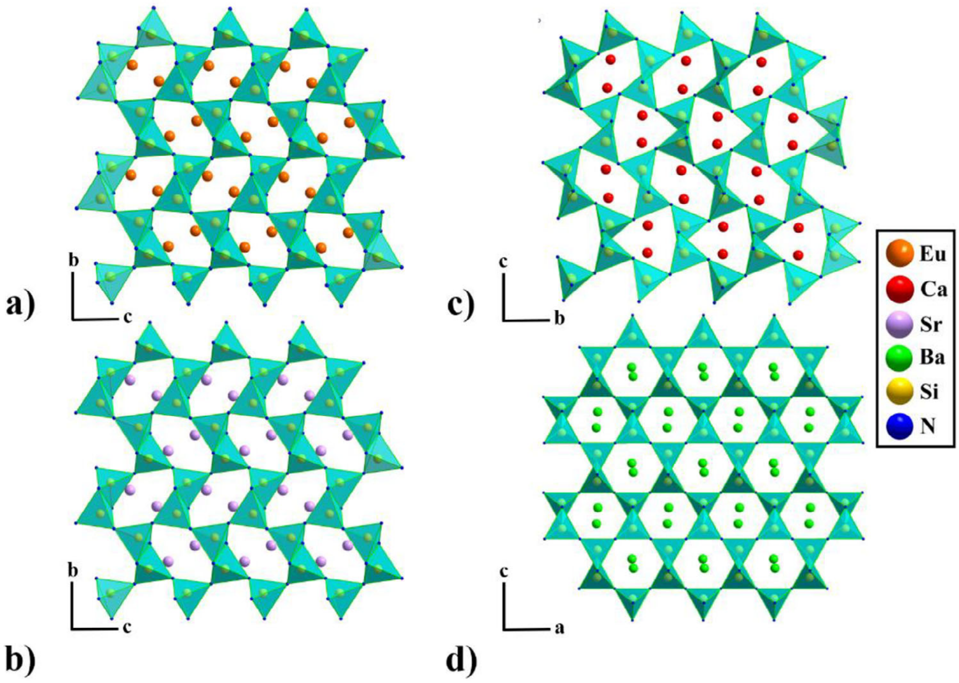

Figure 2. a) $EuSiN_2$ along the [100] direction, b) $SrSiN_2$[10,29] along the [100] direction, c) $CaSiN_2$ [10,12] along the [100] direction, and d) $BaSiN_2$[10,29] along the [010] direction. (Eu atoms are depicted in orange, Ca in red, Sr in violet, Ba in green, Si in yellow, and N in blue).

in distances and angles, due to the very similar ionic radii of Eu^{2+} (1.17 Å) and Sr^{2+} (1.18 Å) (see Figure 2b and 4a and b).

The Eu-N and Sr-N polyhedra, as shown in Figure 4a, b, e, f display the same bow-tie-shaped structure motif resembling those of the edge sharing SiN_4-tetrahedra.

The bow-tie formations of the Eu-N polyhedra exhibit two different Eu-Eu distances, one for in between the edge sharing Eu-N polyhedra (3.46 Å), and one for two neighbouring Eu-N polyhedra (3.36 Å) (see Figure 4a). This feature can be found for the Sr-N polyhedra as well (see Figure 4b).

Even if there is an eightfold nitrogen coordination of the cations, (see Figure 4d) the bow-tie formation of the Eu-N and Sr-N polyhedra has been chosen as it enables an explicit perspective of the layer formation.

The distances between the layers differ only marginally for Eu-Eu (3.46 Å, 3.36 Å) and Sr-Sr (3.47 Å, 3.38 Å). (see Figure 4a and b), as well as the interlayer distances ($EuSiN_2$: 4.04 Å and $SrSiN_2$ 4.03 Å).[10,29]

$BaSiN_2$[10,29] differs not only from the perfect hexagonal formation of the SiN_4-tetrahedra (see Figure 2d), but also features

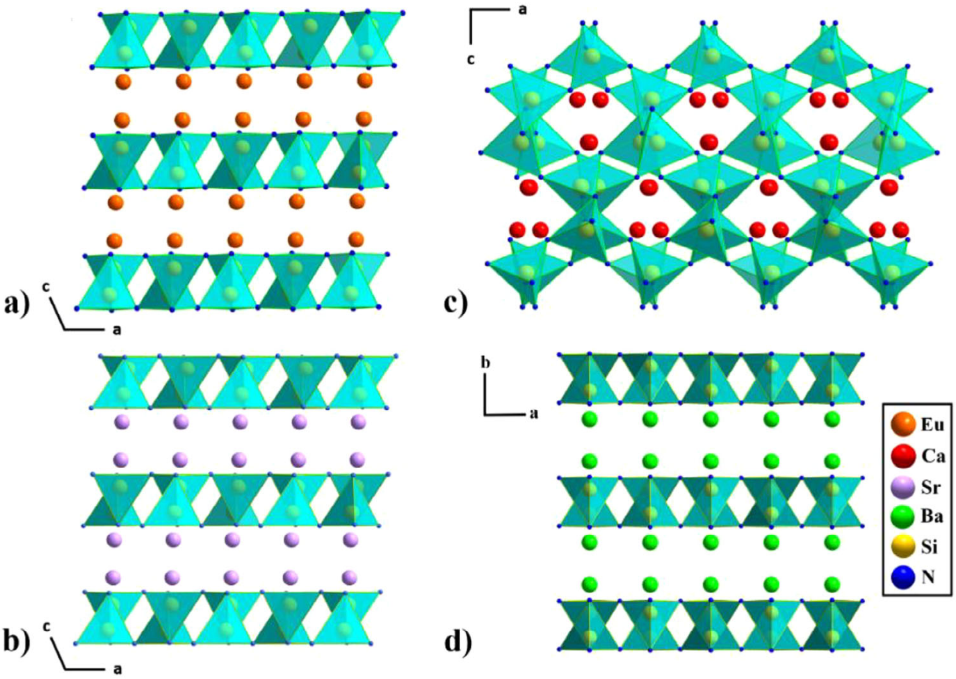

Figure 3. a) $EuSiN_2$ in the [010] direction, b) $SrSiN_2$[10,29] in the [010] direction, c) $CaSiN_2$[10,12] in the [010] direction, and d) $BaSiN_2$[10,29] in the [001] direction. (Eu atoms are depicted in orange, Ca in red, Sr in violet, Ba in green, Si in yellow, and N in blue.).

pentagonal pyramidal Ba-N polyhedra, forming double layers being shifted by one half (see Figure 4c and g). The distance between two Ba atoms is with 3.96 Å much larger than for the neighbouring Eu- and Sr-atoms in $MSiN_2$ (M = Eu, Sr) (see Figure 4a and b), reflecting the decisive influence of the cation. $CaSiN_2$ has not been depicted in Figure 4, as there is no layer formation of the Ca-N polyhedra in $CaSiN_2$.

2.2. Luminescence Properties

The emission and absorption spectra of Eu^{2+} usually consist of broad bands due to transitions between the $^8S_{7/2}$ ($4f^7$) ground state and the crystal field components of the $4f^65d$ excited-state configuration.[59] The characteristics of the f-d luminescence of divalent europium ($4f^7$) in different compositions has been subject of many investigations.[60–62]

The excitation (399 nm, 421 nm, 441 nm, 451 nm, 469 nm, 483 nm, 493 nm) and emission (708 nm, 764 nm) spectra of $EuSiN_2$ are presented in Figure 5a.

They have been recorded two times, once with the excitation wavelength $\lambda_{ex.}$ = 365 nm, and for the second time with $\lambda_{ex.}$ = 469 nm to be sure that the spectra are no artefact and reproducible. The structure in the excitation band of $EuSiN_2$ (see Figure 5a left side) can be ascribed to $4f^7$ to $4f^65d^1$ transition of the Eu^{2+} ion on the single M site. The energy of the Eu^{2+} 4f-5d excitation is strongly dependent on the local environment because of the local coordination and the crystal field splitting of the 5d levels.[63]

If the crystal field is weak and the amount of covalency low, the $4f^65d$ configuration of the Eu^{2+} ion shifts to higher energies and lies therefore above the $^6P_{7/2}$ level which results at low temperatures in a sharp line emission due to the $^6P_{7/2}$ to $^8S_{7/2}$ transition, as it is, e.g., the case for $SrB_4O_7{:}Eu^{2+}$.[64,65] And Figure 5a shows this phenomenon of sharp line emission, which has already been observed several times in literature [29,66–70] for $EuSiN_2$ quite well (see Figure 6, Figure 7 and Figure 9b).

For a comparison the excitation spectra of $SrSiN_2{:}Eu^{2+}$ and $BaSiN_2{:}Eu^{2+}$[29] are depicted in Figure 6a and b. Here, especially for $BaSiN_2{:}Eu^{2+}$,[29] only three dominant peaks are visible. Duan *et al.*[29] claim these peaks are due to the splitting of the 5d bands and because of an overlap only three dominating 5d bands can be observed in the excitation spectra of Eu^{2+}-doped $MSiN_2$ (M = Sr, Ba).[29]

While Poort *et al.*[66] had to perform their measurements of $SrSiO_3$:0.5% Eu^{2+} in 1996 at 4K (see Figure 7a) to get a detailed resolution of the fine structure, we get nowadays an excellent resolution and reliable results with the state-of-the-art photoluminescence spectrometer a room temperature as well[69] (see Figure 5a left side and Figure 7b).

In the CIE 1931 diagram, (see Figure 5b) the chromaticity coordinate positions of $EuSiN_2$ (x = 0.678, y = 0.284) are indicated with a black circle, which corresponds to an intensive red.

The emission spectrum of $EuSiN_2$ consists of two luminescence peaks, one at 708 nm, and the other one at 764 nm (see Figure 5a right side). Having a look into literature we see many compounds as, e.g., $Sr_2Si_5N_8{:}Eu$,[69,71] $Sr_{2-x}La_xSi_{5-x}Al_xN_8{:}Eu^{2+}$[72] and $Ba_{1.89}Eu_{0.11}Si_5N_8$.[70] showing more or less developed shoulders at their luminescence peaks, but observing two fully developed emission peaks is a novel feature for nitridosilicates (see Figure 7b and 9a, b). For $Ba_{0.99}Eu_{0.01}Si_2O_2N_2$[73] having only one Ba site, however, the two luminescence peaks are more distinct.

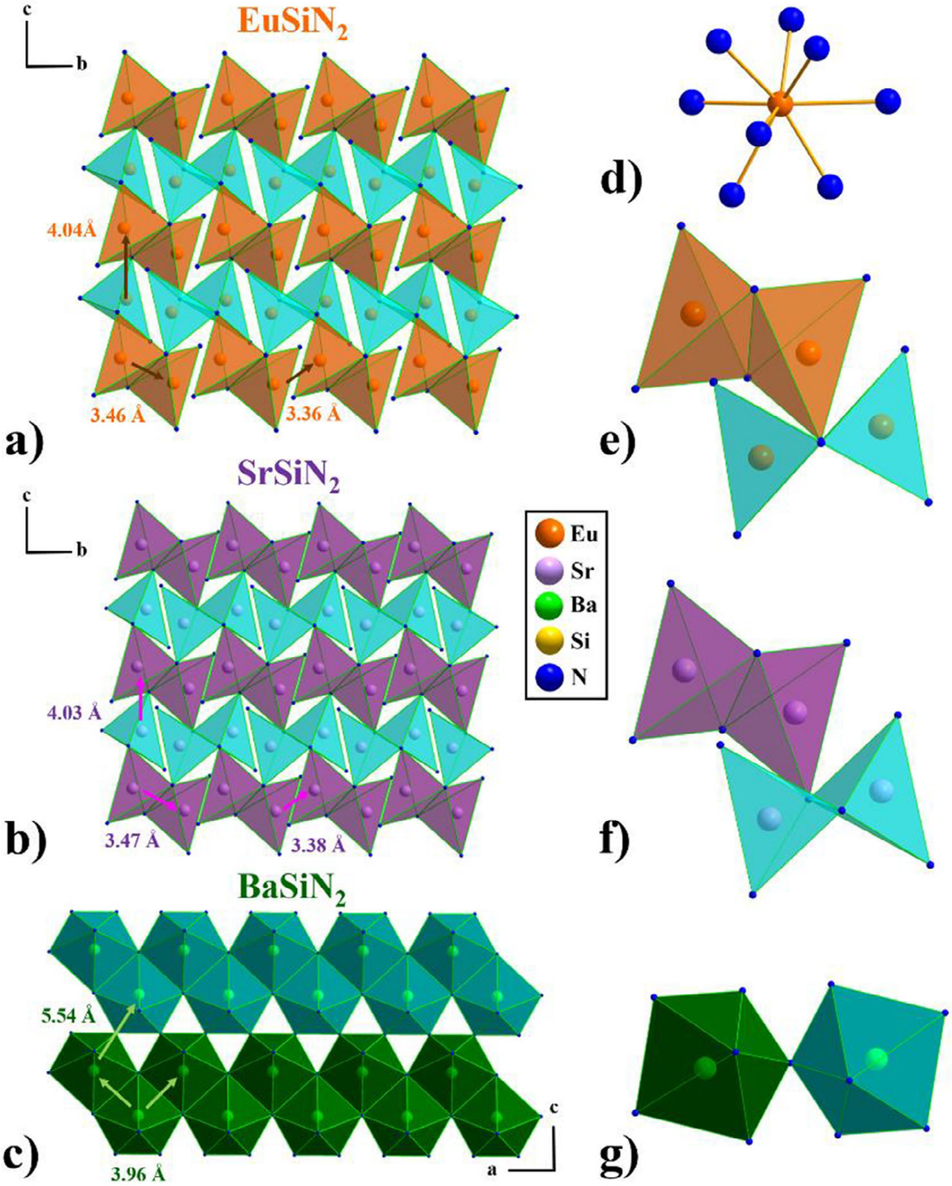

Figure 4. *M*-N polyhedra layers in a) $EuSiN_2$ in the quasi [100] direction (layers in orange and cyan), b) $SrSiN_2$[10,29] in the quasi [100] direction (layers in violet and cyan), and c) $BaSiN_2$[10,29] in the [010] direction (layers in dark green and petrol), d)eightfold nitrogen coordination of the Eu atom, e) bow-tie formation of the Eu-N polyhedra, f) bow-tie formation of the Sr-N polyhedra, and g) pentagonal pyramidal formation of the Ba-N polyhedra. (Eu atoms are depicted in orange, Sr in violet, Ba in green, Si in yellow, and N in blue.).

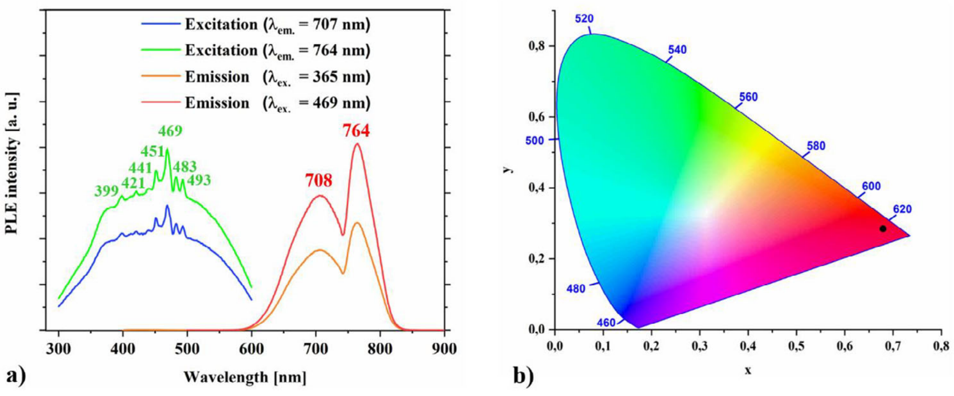

Figure 5. a) Excitation (green and blue) and emission spectra (red and orange) of $EuSiN_2$, b) CIE 1931 diagram of $EuSiN_2$.

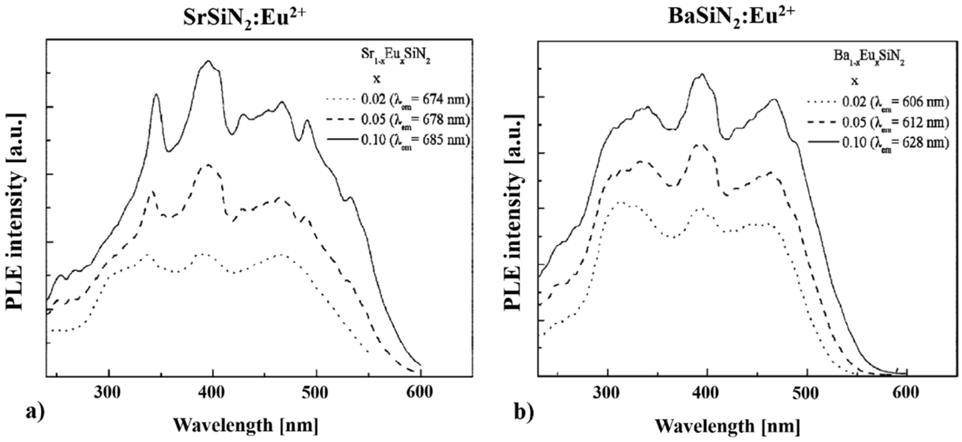

Figure 6. Excitation spectra a) $SrSiN_2:Eu^{2+}$ and b) $BaSiN_2:Eu^{2+}$.[29]

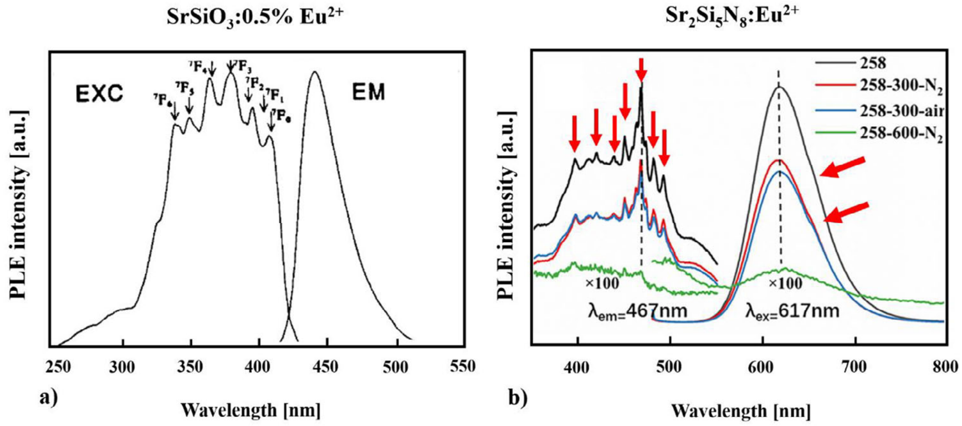

Figure 7. Excitation and emission spectra of a) $SrSiO_3$:0.5% Eu^{2+}[66] and b) $Sr_2Si_5N_8:Eu^{2+}$.[69]

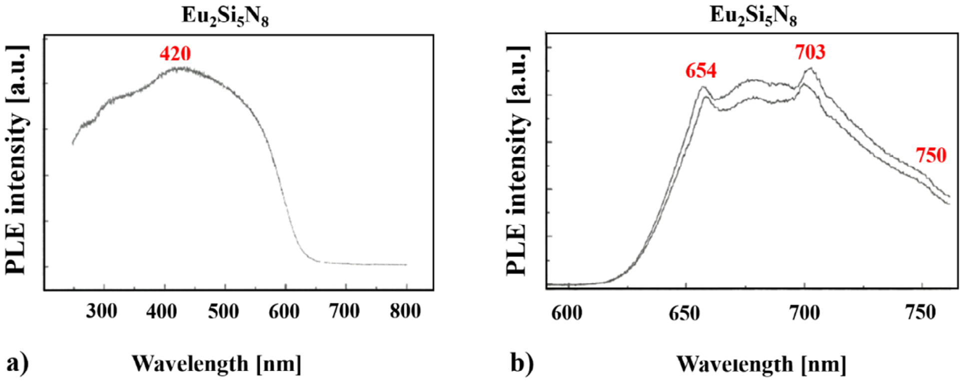

Figure 8. Absorption a) and emission spectra b) of $Eu_2Si_5N_8$.[34,53]

The $5d^1$ orbitals are much more sensitive to the local surrounding than the 4f orbitals. Possible defects or vacancies in the $EuSiN_2$ structure could present a different crystallographic surrounding, strongly reflecting the energy position of the 5d orbitals. Such possibility would give rise to two luminescence peaks.

Another way of classifying this phenomenon is to look at the family compound $Eu_2Si_5N_8$[34,51–53] and the luminescence spectra Huppertz displayed in his dissertation.[53] Here we see clearly that already for $Eu_2Si_5N_8$[34,53] (see Figure 8b) there are two luminescent peaks, one at 654 nm, and the other one at 703 nm. At 750 nm an additional shoulder becomes visible.

Huppertz[53] explains the luminescence peaks of $Eu_2Si_5N_8$[34,53] due to a two-photon absorption of the europium ion. This spectrum was produced by a high-intensity laser with an excitation wavelength of 523.5 nm.

Nonlinear optical behavior investigations (NLO)[74] have been performed for many nitridosilicates including as well

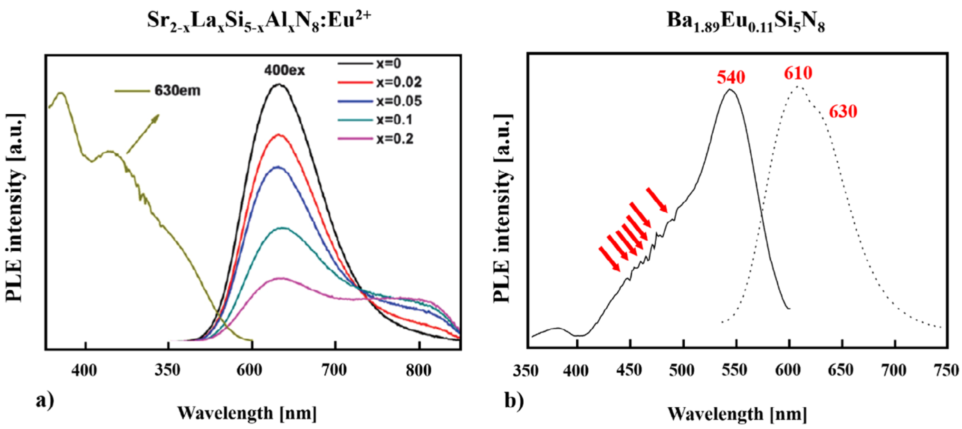

Figure 9. a) Excitation and emission spectra of $Sr_{2-x}La_xSi_{5-x}Al_xN_8:Eu^{2+}$ [72] and b) $Ba_{1.89}Eu_{0.11}Si_5N_8$.[70]

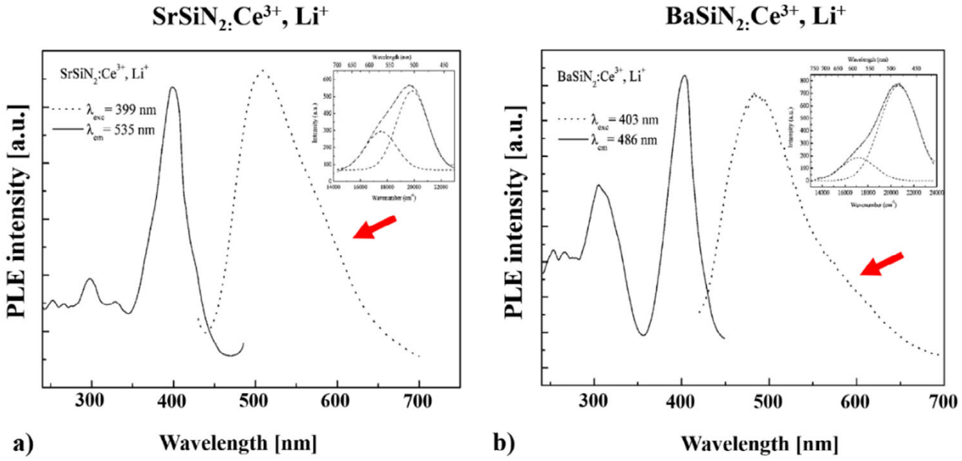

Figure 10. Excitation and emission spectra a) $SrSiN_2:Ce^{3+}$, Li^+[29] and b) $BaSiN_2:Ce^{3+}$, Li^+.[29]

$Eu_2Si_5N_8$.[34,51–53] In the course of this investigations also the two-photon absorption of the Eu^{2+} ion in nitridosilicates played an important role. [34,51–53,70]

Two-photon absorption, being the simultaneous absorption of two photons of identical or different frequencies in order to excite an atom from the ground state via a virtual energy level to a higher excited-electronic state, was originally predicted by Maria Goeppert-Mayer in 1931 in her dissertation,[75] and in 1961 the first experimental verification of the two-photon excitation was found in CaF_2: Eu^{2+}.[76]

$Ba_{2-x}Eu_xSi_5N_8$,[70] revealing long-lasting luminescence and thermoluminescence shows very broad absorption and emission bands being typical for Eu^{2+}. The two emission bands at 610 nm and 630 nm are broadened due to the presence of two overlaying crystallographic Eu^{2+} sites. Höppe *et al.*[70] believed these two neighbouring wavelengths around 600 nm should be mainly due to an efficient two-photon absorption. The exceptional strong red-shift is ascribed to the different nitrogen coordination of the Eu^{2+} ions[51,70] (see Figure 9b and Figure S1).

In $Sr_2Si_5N_8$[72] there are only two types of Sr^{2+} sites for Eu^{2+} substitution, but Figure 9a and Figure S2b show that there are three Gaussian peaks fitting the emission band. Chuang and coworkers[72] assume that the incorporation of La^{3+}- Al^{3+} ions lead to an additional site occupied by Eu^{2+}, not changing the $Sr_2Si_5N_8$ macrostructure, but only modifying the micro-structure around Eu^{2+} in the host lattice. But they do not take into account a possible two-photon absorption for their explanation of the three luminescent peaks. Here as well unusual long-wavelength excitation and emission bands are observed which result from the nitrogen-rich surrounding of the Eu^{2+} ions in $Sr_2Si_5N_8$.

As for the two compounds[51,72] mentioned above, we see for $EuSiN_2$ a very strong red-shift as well. With an eightfold nitrogen coordination of the cations in $EuSiN_2$, like in $SrSiN_2:Eu^{2+}$,[29] we have as well as nitrogen-rich surrounding of the Eu^{2+} ions.

For $SrSiN_2:Ce^{3+}$, Li^+ as well as $BaSiN_2:Ce^{3+}$, Li^{+}[29] a shoulder in their emission spectra appears as well, (see Figure 10) but two fully generated luminescence peaks are only distinctive for $EuSiN_2$. The inserted pictures in Figure 10 shows that these peaks can be fitted very well with two Gaussian functions, which proves the presence of the shoulder. However Duan *et al.*[29] provide no explanation for this feature. For the Eu-doped compounds, $SrSiN_2:Eu^{2+}$[29] and $BaSiN_2:Eu^{2+}$,[29] no shoulder can be detected in the emission spectrum, only for $Ba_{1-x}Eu_xSiN_2:Eu^{2+}$[29] ($x = 0.1$) a very first sign of a possible shoulder is implied (see Figure S3).

3. Conclusions

With $EuSiN_2$ a novel Eu-nitridosilicate is presented including a very comprehensive structure description and a comparison with its related compounds $MSiN_2$ (M = Ca, Sr, Ba). A different way of presenting the structure as M-N polyhedra layers is introduced. Furthermore, the luminescence characteristics of $EuSiN_2$ are studied.

The phenomenon of sharp peaks in the excitation band of $EuSiN_2$ can be ascribed from $4f^7$ to $4f^65d^1$ transition of the Eu^{2+} ion and has already been observed several times in literature. In former times, it was necessary to cool down the sample to very low temperatures to get a detailed structure of the excitation bands. Nowadays, state-of-art photoluminescence spectrometer provide an excellent resolution and reliable results in room temperature as well.

The emission spectrum of $EuSiN_2$ consists of two luminescence peaks, one at 708 nm, and the other one at 764 nm.

Having a look into literature, many europium-doped nitridosilicates exhibit more or less developed shoulders for their luminescence peaks, but two clearly shaped emission peaks are a novel feature for nitridosilicates.

For the family compound $Eu_2Si_5N_8$ two luminescent peaks can be found as well, and Huppertz explained them by a two-photon absorption of the Eu^{2+} ion. Also $Ba_{1.89}Eu_{0.11}Si_5N_8$ shows this phenomenon and Höppe argues with an efficient two-photon absorption too. Höppe also proposes that, the two luminescent peaks could be caused by two overlaying crystallographic Eu sites. $EuSiN_2$ has only one crystallographic site, which makes the two-photon absorption more probable.

But we cannot rule out that possible defects and vacancies could influence the $5d^1$ orbitals presenting a different crystallographic surrounding for the Eu ion and giving rise to the two luminescence peaks.

Therefore, we would like to concur with the explanation of Huppertz and Höppe and propose likewise a two-photon absorption for $EuSiN_2$ being the reason for the two distinct luminescence peaks in the emission spectrum.

But to be absolutely sure that the high intense laser light is needed, and the two-photon absorption could not perhaps take place with excitation light of lower intensity as well this will be part of a future project.

This luminescence feature is not only present for the 2-5-8 phases, but already visible for Sr- and $BaSiN_2$:Ce^{3+},Li^+ as well, having a shoulder at their luminescence peaks.

As alkaline-earth silicon nitrides $MSiN_2$ (M = Sr, Ba) have been already several times investigated because of their electronic properties, especially their band gap features e.g. as semiconductors, it would be very interesting to investigate the nonlinear optical behavior of $EuSiN_2$ in a future project, just as the magnetism of the Europium will be a subject of further studies.

4. Experimental Section

All sample handlings were performed in an inert atmosphere using an argon-filled glove box (MBraun Labmaster, $\rho(O_2) / \rho o < 0.1$ ppm, $\rho(H_2O) / \rho o < 0.1$ ppm) due to the extreme sensitivity of both the starting materials and some of the final products to moisture and air.

Synthesis of EuN: For the synthesis of EuN, Eu (Hunan Rare Earth Metals Materials Co, 99.9%) was put in a tungsten crucible, placed into a water-cooled quartz reactor and mounted into a radio-frequency furnace[77] under flowing N_2 atmosphere (Nippon Gases 99.999%, purified with an oxysorb cartridge (Messer Griesheim)) of ambient pressure for 30 minutes at maximally 850 °C. Great care has been taken, that the Eu does not melt prior or during the early stages of the reaction. After the reaction, the sample was finely ground in an agate mortar and sieved (100 mesh).

Synthesis of $EuSiN_2$: For the synthesis of $EuSiN_2$ a mixture of 433.27 mg EuN and 69.37 mg Si_3N_4 (β-Si_3N_4, Chempur 99.999%), were mixed in an agate mortar and pressed into a pellet with 8 or 10 mm diameter.

The pellet was placed into a tantalum crucible under argon atmosphere in a glovebox and the set up was placed into a water-cooled quartz reactor of a radio-frequency furnace[77] and hold at 1550 °C for 20 minutes under nitrogen atmosphere (Equation (1)). By this reaction a dark red powder was obtained.

X-ray diffraction: X-ray diffraction experiments on $EuSiN_2$ powder samples were performed on a STOE STADI P powder diffractometer in Debye-Scherrer geometry with Ge (111)-monochromatized Co-$K\alpha_1$ radiation (λ = 1.788965 Å). The samples were enclosed in a glass capillary of 0.3 mm diameter.

The deposition number CSD-2435060 for $EuSiN_2$ (https://www.ccdc.cam.ac.uk/services/structures?id = https://doi.org/10.1002/chem.202404395) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe (http://www.ccdc.cam.ac.uk/structures).

Luminescence: Steady-state emission and excitation spectra presented in this study have been recorded using the Fluorolog-QM photoluminescence (PL) spectrometer from HORIBA scientific working with a continuous 75 W Xe lamp and a cooled Hamamatsu R928P photomultiplier in TE-cooled housing. The emission and excitation spectra were corrected for the instrumental artefacts using the supplied correction factors. A 400 nm long pass filter was used to eliminate the second order artefacts.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: europium (II) · luminescence · nitridosilicates · NLO materials · rare earth

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