Missing Member in the $M^{II}M^{IV}Si_{2}N_{7}$ Compound Class: Carbothermal Reduction and Nitridation Synthesis Reveal Substitution of Nitrogen by Carbon and Oxygen in CaLu$[Si_{4}N_{7−2x}C_{x}O_{x}⁺]$:Eu$^{2+}$/Ce$^{3+}$ ($x \approx 0.3$)

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Abstract: The nitridosilicate CaLu$[Si_{2}N_{7−2x}C_{x}O_{x}⁺]$ ($x \approx 0.3$) was synthesized by carbothermal reduction and nitridation starting from CaH$_{2}$, Lu$_{2}$O$_{3}$ graphite and amorphous Si$_{3}$N$_{4}$ at 1550°C in a radiofrequency furnace. CaLu$[Si_{2}N_{7−2x}C_{x}O_{x}⁺]$ ($x \approx 0.3$) crystallizes isotypically to many previously known $M^{II}M^{IV}Si_{2}N_{7}$ compounds in the space group P6$_{3}$mc, as was confirmed by Rietveld refinement based on powder X-ray diffraction data. Incorporation of carbon into the crystal structure as a result of the carbothermal synthesis route was confirmed by $^{13}$C and $^{29}$Si MAS NMR spectroscopy. For the first time in the $M^{II}M^{IV}Si_{2}N_{7}$ compound class, complementary EDX measurements suggest that simultaneous incorporation of oxygen compensates for the negative charge excess induced by carbon, resulting in an adjusted sum formula, CaLu$[Si_{2}N_{7−2x}C_{x}O_{x}⁺]$ ($x \approx 0.3$). When excited with UV-to-blue light, CaLu$[Si_{2}N_{7−2x}C_{x}O_{x}⁺]$ ($x \approx 0.3$) shows an emission maximum in the blue spectral region ($\lambda_{em} = 484$ nm; fwhm = 4531 cm$^{-1}$) upon doping with Ce$^{3+}$, whereas Eu$^{2+}$-doped CaLu$[Si_{2}N_{7−2x}C_{x}O_{x}⁺]$ ($x \approx 0.3$) exhibits a yellow-green emission ($\lambda_{em} = 546$ nm; fwhm = 3999 cm$^{-1}$).

Introduction

Several compounds with the stoichiometric formula $M^{II}M^{IV}Si_{2}N_{7}$ have been investigated in recent years. Most $M^{II}M^{IV}Si_{2}N_{7}$ compounds with differently sized $M^{II}$ and $M^{IV}$ cations crystallize in the hexagonal space group P6$_{3}$mc, whereas lower symmetric orthorhombic space groups are predominantly observed when both $M^{II}$ and $M^{IV}$ cations are of comparable size.[11–13] Compounds containing Al$^{3+}$ crystallize in the orthorhombic space group Pna$_{2}$, owing to the fact that aluminium does not act as a counter ion but is incorporated in the form of [AlN$_{4}$] tetrahedra into the anionic network, leading to nitridoalumosilicates.[14–16] Different synthetic strategies have been applied to facilitate the synthesis of the various $M^{II}M^{IV}Si_{2}N_{7}$ compounds. Most Sr$^{2+}$ and Ba$^{2+}$ containing compounds have been obtained starting from metals or nitrides.[1–3,5–7,10,13] However, compounds with $M^{IV} = Ca^{2+}$ in particular were not successfully synthesized by applying this approach due to the decreasing cation size going from Ba$^{2+}$ to Ca$^{2+}$, thus limiting access to CaM$^{IV}Si_{2}N_{7}$ compounds.[9,11,13] Therefore, only a few examples obtained by other synthetic strategies are known. CaM$^{IV}Si_{2}N_{7}$ ($M^{IV} = Y, Sc$) was exclusively synthesized by carbothermal reduction and nitridation (CRN) with elemental carbon as reducing agent to facilitate the reaction.[9,6,11,12] Carbon either acted as an impurity phase or was incorporated into the structures; this can be investigated by $^{13}$C magic-angle spinning (MAS) NMR spectroscopy. In order to compensate the negative charge excess caused by an incorporation of C$^{−}$ onto the N$^{−}$ sites, an equimolar substitution of $M^{IV}$ by $M^{II}$ was assumed.[9,6,11,12]

The $M^{III}Si_{2}N_{7}$ compound class does not only offer interesting structural features like star shaped [N[4][SiN]$_{4}$] units containing a fourfold bridging ammonium-type nitrogen, but also provides doping possibilities for both application relevant rare earth activator ions Eu$^{2+}$ and Ce$^{3+}$ due to similar sizes and charges compared to the $M^{IV}$ and $M^{II}$ cations, respectively. Doping $M^{IV}Si_{2}N_{7}$ with Eu$^{2+}$ was shown to result in green to yellow emission whereas Ce$^{3+}$-doped compounds exhibit emission in the blue spectral region.[6,7,11–16] Doped compounds can exhibit interesting luminescence properties relevant for application in one or two phosphor-converted light emitting diodes (1/2pcLEDs) in the lighting and display industries. The first, and so far most widely used, phosphor in white 1pcLEDs is $Y_{2}O_{3}:GdAl_{2}O_{3}:Ce^{3+}$ (YAG:Ce$^{3+}$), whose yellow emission combined with a blue-emitting (In,Ga)N primary LED, for which the 2014 Nobel Prize in Physics was awarded to Akasaki, Amano and Nakamura, leads to cold white light.[17,18] Blue phosphors with a broad emission band could be used to cover the blue-cyan gap between the spectrum of a narrow-emitting near-UV...
primary LED and the emission of a yellow phosphor or green-red phosphor mixture, leading to high color quality and making the near UV primary LEDs more appealing.\(^{[16,20]}\)

The CRN synthesis method offers the advantage of using commonly available and stable starting materials, which makes it suitable for mass production, and provides access to compounds that are not accessible by other synthetic routes so far. Therefore, this method, besides other synthetic approaches, could enable the synthesis of previously unknown host structures or compounds for rare earth doping to develop novel luminescent materials.

In this contribution, we report on the CRN synthesis of CaLu\([Si(N_2)_2C_4O_4]\) \((x \approx 0.3)\), a previously not observed, missing member of the \(M^+\)\(M^2\)\(SiN\) compound class. CaLu\([Si(N_2)_2C_4O_4]\) \((x \approx 0.3)\) was investigated by \(^{1}C\) and \(^{29}Si\) MAS NMR spectroscopy to specify the incorporation of carbon. Through the combination of NMR and elemental analysis, the simultaneous incorporation of oxygen rather than the previously assumed substitution of \(M^2\) by \(M^1\) was specified. This makes CaLu\([Si(N_2)_2C_4O_4]\) the first oxonitridocarbidosilicate in this compound class and just the second oxonitridocarbidosilicate besides \(RE\text{Ba}_2\text{Sr}_2\text{Ti}_4\text{O}_{13}\)\((RE = Lu, Y)\) known so far.\(^{[21]}\) Additional luminescence investigations reveal emission in the yellow-green and blue spectral regions upon doping with either Eu\(^{2+}\) or Ce\(^{3+}\), respectively.

### Results and Discussion

#### Synthesis and chemical analysis

CaLu\([Si(N_2)_2C_4O_4]\) \((x \approx 0.3)\) was obtained by carbothermal reduction and nitridation according to Equation (1) when using carbon as a reducing agent.

\[
\text{CaH}_2 + \frac{1}{2} \text{Lu}_2\text{O}_3 + \frac{3}{4} \text{Si}\text{N}_4 + \frac{3}{2} \text{C} + \frac{11}{15} \text{N}_2 \rightarrow \text{CaLuSi}_x\text{N}_{4-x}\text{C}_y\text{O}_{3-y} + \frac{3}{4} \text{NH}_3 + \frac{5}{2} \text{CO}
\]

As the reaction yielded a fine powder, the structure and phase purity of the obtained product was confirmed by Rietveld refinement based on powder X-ray diffraction (PXRD) data, for which literature known isotopic SrYbSi\(_4\)\(^{[2]}\) served as a starting model. As shown in Figure 1, the observed and calculated XRD profiles match well, with reasonable values of the reliability factors.

Crystallographic data from the Rietveld refinement are given in Table 1, while Wyckoff positions, atomic coordinates and isotropic displacement parameters are listed in Table S1 in the Supporting Information.

Despite the use of stoichiometric amounts of carbon and oxygen in the starting materials to avoid impurities as carbon and oxygen are ideally withdrawn from the reaction in form of gaseous CO, the synthesis yielded grayish powders. A yellow-grayish powder with yellow-green luminescence was obtained upon doping with Eu\(^{2+}\) while doping with Ce\(^{3+}\) led to a white-grayish powder with blue luminescence, respectively. SEM- and TEM-EDX measurements (Tables S2 and S3; Figure S1a) are in good agreement with each other and with the theoretical values. Both investigations revealed an atomic Ca/Lu ratio of about 1:1 and in each case very similar values for oxygen. Furthermore, TEM investigations have shown values for carbon also resulting in an atomic C/O ratio of about 1:1. However, as the products have a grayish tint, the carbon content could originate from the sample itself as well as from an amorphous carbon side phase. To exclude that carbon remained as a side phase, the products obtained by the CRN method were purified through oxidation of remaining carbon by heating the material in a muffle furnace for 24 h at 800 °C under air. This resulted in optically more lucid products with brighter luminescence but without a grayish tint. As can be seen in the luminescence spectra by the absence of line emission, Eu\(^{2+}\) was not oxidized to Eu\(^{3+}\) in this purification process. This can be explained by the

![Figure 1: Rietveld refinement for CaLu\([Si(N_2)_2C_4O_4]\) \((x \approx 0.3)\) with observed (black) and calculated (red) powder X-ray diffraction patterns and the corresponding difference profile (gray). Vertical blue bars indicate the position of the Bragg reflections of the title compound.](image)

### Table 1. Details of the Rietveld refinement of CaLu\([Si(N_2)_2C_4O_4]\) \((x \approx 0.3)\)

| Parameter                          | Value                          |
|-----------------------------------|--------------------------------|
| Formula weight/g mol\(^{-1}\)     | 425.433                        |
| Crystal system                    | hexagonal                      |
| Space group                       | P6\(\bar{3}c\) (no. 186)       |
| Lattice parameters/Å               | 9.7392(1)                      |
| Density/g cm\(^{-3}\)              | 4.7131                         |
| Diffractometer                    | STOE Stadi P                   |
| Detector                          | Mythen 1 K                     |
| Radiation                         | Cu–Kα (\(λ = 1.5406\) Å)       |
| Monochromator                     | Ge(111)                        |
| 2θ range/°                        | 5 ≤ 2θ ≤ 95                    |
| Data points                       | 6042                           |
| Total number of reflections       | 70                             |
| Refined parameters                | 49                             |
| Background function               | Chebychev polynomial (12 terms) |
| \(R\) values                      | \(R = 0.0408\)                 |
| \(R_{wp}\)                        | 0.0564                         |
| \(R_{exp}\)                       | 0.0232                         |
| Goodness of fit                   | 2.4241                         |
fact that $\text{Eu}^{2+}$, which is larger than $\text{Eu}^{3+}$, occupies the large Ca site and is thus stabilized in its oxidation state. In addition, $\text{Eu}^{2+}$ is mainly coordinated by $\text{N}^-$, which is known to have a certain degree of reducing potential.\(^{[22]}\)

EDX measurements (Figure S1b, Table S4) show increased oxygen content caused by superficially bound oxygen. CHNS analysis (Table S5) was used for quantification of the carbon content. As a certain carbon content could still be determined despite purification, it was assumed that carbon is no longer present as a secondary phase, but has also been incorporated into the structure. In order to confirm the carbon incorporation, NMR spectroscopy was performed. In addition, CHNS analysis shows the absence of hydrogen in the sample.

**Structure description**

$\text{CaLu}_2\text{Si}_3\text{N}_7\text{C}_2\text{O}_{13}$ ($\chi \approx 0.3$) crystallizes like many other representatives of the $M^+M'^+\text{Si}_3\text{N}_4$ compound class in hexagonal space group $P6_3/mc$.\(^{[13–17]}\) The structure exhibits a three-dimensional network of all-side vertex-sharing $\text{Si}_4$ tetrahedra. Four tetrahedra are linked via one common fourfold bridging (N,C)\(^{[4]}\) to form a star shaped unit, which was first reported by Huppertz et al. for $\text{BaYbSi}_3\text{N}_7$ (Figure 2a).\(^{[1]}\) These [($\text{N,C}$)\(^{[4]}\)(Si(N,O)\(^{[2]}\))]\(_4\) units are all-side vertex sharing and stacked along the [001], leading to a $[\text{Si}_4\text{N}_3\text{O}_2\text{C}_2\text{O}_5]$ network. Stacking and linking the star shaped units leads to dreier and sechser ring channels along [010] with $\text{Ca}^{2+}$ and $\text{Lu}^{3+}$ located in the distorted sechser ring channels (Figure 2b).\(^{[20]}\) The one crystallographic $\text{Lu}^{3+}$ site is thereby octahedrally coordinated by six (N,O)\(^{[2]}\) while twelve (N,O)\(^{[2]}\) coordinate the only crystallographic $\text{Ca}^{2+}$ site in form of an anti-cuboctahedron (Figure 3).

The interatomic $\text{Si}^-$–(N,O)\(^{[2]}\) distances in the anionic network range from 1.676(7) to 1.746(6) Å while the $\text{Si}^-$–(N,C)\(^{[4]}\) distances are between 1.868(2) and 1.891(6) Å. The slightly elongated bonds result from the repulsion of formally positively charged N\(^{[4]}\) and positively polarized Si. Lu$^-$–(N,O) and Ca$^-$–(N,O) distances vary from 2.296(7) to 2.315(7) Å and 2.819(6) to 2.983(7) Å, respectively. The observed distances are in good agreement with the reported values from other $M^+M'^+\text{Si}_3\text{N}_4$ compounds.\(^{[1–3,5–7,11,12]}\)

**NMR spectroscopy**

$^{13}$C and $^{29}$Si MAS NMR experiments were conducted to determine the incorporation of carbon into the tetrahedral network. The star shaped unit [N3\(^{[4]}\)(Si(N,O)\(^{[2]}\))] (for detailed atom assignment see Figure S2) consists of one [Si1(N2),N3] and three [Si2(N1),N2 N3] tetrahedra connected via N3\(^{[4]}\). N1\(^{[2]}\) and N2\(^{[2]}\) are suitable for substitution by O, while C can be incorporated onto the N3\(^{[4]}\) site, which leads to [Si1(N2)\(_{\text{III}}\)N3\(_{\text{III}}\)C and Si2(N1),N2(N1\(_{\text{III}}\),C3)]. The $^{13}$C NMR spectrum (Figure 4) shows one narrow peak corresponding to an isotropic chemical shift of about 32 ppm, which is consistent with the expectation of the one possible C site [C3\(_{\text{III}}\)(Si(N,O))] and matches with the value reported in literature.\(^{[1]}\)

Two signals with very similar chemical shift and an intensity ratio of 1:3 are expected in the $^{29}$Si NMR spectrum. The slightly different chemical shifts originate from marginally different Si–N3 distances (Si1–N3: 1.868(2) Å, Si2–N3: 1.891(6) Å) but otherwise similar chemical surroundings. Partial substitution of N3 by C would lead to two additional signals shifted towards larger chemical shift values.\(^{[24]}\) Figure 5 shows the obtained $^{29}$Si

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**Figure 2.** a) A star-shaped [($\text{N,C}$)\(^{[4]}\)(Si(N,O)\(^{[2]}\))]\(_4\) unit and b) crystal structure of CaLu$_2$Si$_3$N$_7$C$_2$O$_{13}$ ($\chi \approx 0.3$). Si(N,C,O)$_4$ tetrahedra in blue, Ca atoms yellow, Lu atoms light gray.

**Figure 3.** Coordination spheres of a) Lu and b) Ca. N/O atoms blue/red, Lu light gray, Ca yellow.

**Figure 4.** $^{13}$C MAS NMR spectrum of polycrystalline CaLu$_2$Si$_3$N$_7$C$_2$O$_{13}$ ($\chi \approx 0.3$), acquired at the MAS frequency of 10 kHz.
assume charge compensation through substitution of $M'$ by $M''$ shown by EDX measurements of the $M'/M''$Si ratios, which revealed an excess of $M''$. However, no statements were made on the possibility of oxygen incorporation despite using oxides or carbonates as starting materials.[8,9] Therefore, CaLu[Si$_{4}$N$_{2}$O$_{3}$] ($x \approx 0.3$) is the first oxonitridocarbidosilicate described in this compound class and only the second literature known oxonitridocarbidosilicate so far.[21]

**UV/Vis reflectance spectroscopy**

The optical band gap of undoped CaLu[Si$_{4}$N$_{2}$O$_{3}$] ($x \approx 0.3$) was determined using solid-state UV/Vis spectroscopy. The measured diffuse reflectance spectrum was transformed into a pseudo-absorption spectrum using the Kubelka-Munk function $R(R) = (1 - R)^2/2R$ with $R$ being the measured reflectance.[25] The optical band gap was determined from a Tauc plot, where $hv$ is plotted against $(F(R) - h\nu)^{1/2}$ with $n = 1/2$ for a direct allowed transition by intersecting the aligned tangent on the linear region with the abscissa.[26] Thereby, the optical band gap was estimated to be approximately 4.5 eV (Figure 7), which makes CaLu[Si$_{4}$N$_{2}$O$_{3}$] ($x \approx 0.3$) a suitable host material for doping, as wide band gaps $\geq 4$ eV are desired for pcLED applications.[27,28] This is in good agreement with band gap values obtained for other $M'M''$Si$_{4}$N$_{2}$ compounds.[3,21]

**Luminescence**

Due to similar sizes and charges compared to Ca$^{2+}$ and Lu$^{3+}$, doping with both rare earth activator ions Eu$^{2+}$ and Ce$^{3+}$, respectively, is feasible. A comparison of charges and ionic radii indicates that Ce$^{3+}$ (r(coordination number CN: 6) = 1.01 Å) preferably occupies the octahedrally coordinated Lu$^{3+}$ site (r(CN: 6) = 0.861 Å) while the larger Eu$^{2+}$ (r(CN: 10) = 1.35 Å) prefers the anti-cuboctahedral Ca$^{2+}$ (r(CN: 12) = 1.34 Å) site.[29]

**Figure 5.** Acquired $^{29}$Si MAS NMR spectrum (black, MAS frequency: 10 kHz) of polycrystalline CaLu[Si$_{4}$N$_{2}$O$_{3}$] ($x \approx 0.3$) along with four deconvoluted Lorentz functions (red) and the corresponding calculated fit (blue).

**Figure 6.** Detailed analysis of the deconvoluted $^{29}$Si MAS NMR spectrum of polycrystalline CaLu[Si$_{4}$N$_{2}$O$_{3}$] ($x \approx 0.3$) by four Lorentz functions.

**Figure 7.** Tauc plot ($n = 1/2$) for an undoped CaLu[Si$_{4}$N$_{2}$O$_{3}$] ($x \approx 0.3$) powder sample.
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Comparing the luminescence properties of CaLu[Si$_{4}$N$_{7}$C$_{2}$O$_{4}$]Eu$^{2+}$ ($\lambda_{em}$ = 546 nm and a fwhm of about 118 nm/3600 cm$^{-1}$) with known phosphors shows that CaLuSi$_{4}$N$_{7}$Eu$^{2+}$ has very similar characteristics as broadband green-yellow emitting Y$_{3}$Al$_{5}$Ga$_{2}$O$_{12}$:Ce$^{3+}$ (YAG:Ce$^{3+}$, Lumileds Phosphor Center Aachen) with its emission maximum at $\lambda_{em}$ = 552 nm ($\lambda_{em}$ = 440 nm) and fwhm of 118 nm/3600 cm$^{-1}$ (Figure S6). YAG:Ce$^{3+}$ shows a relative photoemission intensity at 150°C of about 53% compared to room temperature.$^{[12,17,43]}$

It is most commonly used in state-of-the-art white-light single phosphor-converted light-emitting diodes (1pcLEDs), which could therefore also be a possible application for CaLuSi$_{4}$N$_{7}$Eu$^{2+}$. Its narrow excitation band could also be an interesting feature for an application as a color point stabilizer in LEDs.

**Conclusion**

In this contribution, we have reported the luminescence properties of Eu$^{2+}$- and Ce$^{3+}$-activated CaLu[Si$_{4}$N$_{7}$C$_{2}$O$_{4}$] (x ≈ 0.3) synthesized by carbothermal reduction and nitridation, which is the only method to facilitate the formation of CaM$^{2+}$Si$_{4}$N$_{7}$ so far. CaLu[Si$_{4}$N$_{7}$C$_{2}$O$_{4}$] (x ≈ 0.3) crystallizes isotypically to many previously known M$^{2+}$M$^{3+}$Si$_{4}$N$_{7}$ compounds in space group P6$_{3}$mc. As carbon was used as a starting material, $^{13}$C and $^{29}$Si MAS NMR spectroscopy were used to determine the incorporation of carbon into the tetrahedron network. Prior to this, the samples were purified by heating under air to remove residual carbon, which leads to optically more lucid powders with brighter luminescence. Analysis shows a partial substitution of N$^{3-}$ by C$^{3-}$ on the fourfold bridging N$^{2-}$ site. Combining NMR spectroscopy with elemental analyses like EDX and CHNS leads to the assumption that the negative charge excess caused by the incorporation of C$^{3-}$ is compensated for by equimolar incorporation of O$^{2-}$ rather than by substitution of M$^{2+}$ onto the M$^{3+}$ site, as reported for other M$^{2+}$M$^{3+}$Si$_{4}$N$_{7}$ compounds synthesized by the CRN method. This leads to an actual composition close to CaLuSi$_{4}$N$_{7}$O$_{6}$C$_{3}$O$_{3}$, thus making this the only oxonitridocarboasilicate in this compound class as well as only the second oxonitridocarboasilicate in general. As CRN is the only method for the synthesis of CaM$^{2+}$Si$_{4}$N$_{7}$ known so far, carbon incorporation and therefore a possible stabilization of the crystal structure by more covalent Si–C bonds, which leads to a higher rigidity and stability of the network despite the incorporation of a smaller M$^{3+}$ cation, might be essential for the formation of other CaM$^{2+}$Si$_{4}$N$_{7}$ compounds. Because of the presence of M$^{2+}$ and M$^{3+}$ sites, doping with Eu$^{2+}$ as well as Ce$^{3+}$ is possible. The latter leads to an emission maximum at $\lambda_{em}$ ≈ 484 nm and a fwhm of about 118 nm/3600 cm$^{-1}$ upon irradiation with UV-to-blue light ($\lambda_{ex}$ = 400 nm). Purified CaLu[Si$_{4}$N$_{7}$C$_{2}$O$_{4}$]Eu$^{2+}$ ($\lambda_{em}$ = 546 nm and a fwhm of about 118 nm/3600 cm$^{-1}$), which can be compared to those of commercially used YAG:Ce$^{3+}$. Both Eu$^{2+}$- and Ce$^{3+}$-doped phosphors offer properties that could be relevant for applications. As the M$^{2+}$M$^{3+}$Si$_{4}$N$_{7}$ compound class offers a variety...
Experimental Section

Synthesis: Due to the air and moisture sensitivity of CaH₂, all manipulations were carried out under argon either in an Ar-filled glovebox (Unilab, MBraun, Garching; O₂ < 1 ppm; H₂O < 1 ppm) or in an Ar-filled glovebox by applying the Schlenk technique. Calu[Si₃N₃(C₂O₄)₃] (x ≈ 0.3) was synthesized starting from 29.7 mg CaH₂ (0.705 mmol, Sigma-Aldrich, 99.99 %), 104.3 mg Lu₂O₃ (0.353 mmol, Sigma-Aldrich, 99.9 %), 131.9 mg amorphous Si₃N₄ (0.940 mmol, Ube Industries, SNA-00), 12.7 mg graphite (1.058 mmol, Chempur, 99.9 %) and either EuF₃ (0.353 mmol, Sigma-Aldrich, 99.99 %) or CeF₃ (Sigma-Aldrich, 99.99 %) as dopants. The starting materials were thoroughly ground in an agate mortar and filled into a tungsten crucible, which was then transferred into a water-cooled silica glass reactor of a radiofrequency furnace (TIG 10/100; Hüttigerring Elektronik Freiburg, Germany) attached to a Schlenk line. The crucible was heated under N₂ to 1550°C within 1 h, maintained at that temperature for 2 h, cooled down to 500°C within 2 h, and finally, the product was quenched by switching off the furnace.[44–46] Upon doping with Eu³⁺, the product was obtained as a yellow-grayish powder with yellow-green luminescence when excited with UV-to-blue light. Ce³⁺ doping led to a white-grayish powder, which shows blue luminescence upon irradiation with UV to blue light. In order to remove residual carbon, which led to the grayish tint of the products, the powders were heated under air in a muffle furnace for one day at 800°C. This purification led to optically more lucid powders with no grayish tint and brighter luminescence.

Powder X-ray diffraction: Powder X-ray diffraction (PXRD) data of the ground products sealed into glass capillaries (0.2 mm diameter, 2 mm cooled silica glass reactor of a radiofrequency furnace (TIG 10/100; Hüttigerring Elektronik Freiburg, Germany) attached to a Schlenk line. The crucible was heated under N₂ to 1550°C within 1 h, maintained at that temperature for 2 h, cooled down to 500°C within 2 h, and finally, the product was quenched by switching off the furnace.[44–46] Upon doping with Eu³⁺, the product was obtained as a yellow-grayish powder with yellow-green luminescence when excited with UV-to-blue light. Ce³⁺ doping led to a white-grayish powder, which shows blue luminescence upon irradiation with UV to blue light. In order to remove residual carbon, which led to the grayish tint of the products, the powders were heated under air in a muffle furnace for one day at 800°C. This purification led to optically more lucid powders with no grayish tint and brighter luminescence.

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Transmission electron microscopy (TEM): For TEM-EDX, the sample was ground, suspended in ethanol and drop-cast on a copper grid with holey carbon film (S160NH2C, Plano GmbH, Wezlar, Germany), which was then fixed on a double-tile low-background holder. The measurements were performed with a Titan 80–300 (FEI, USA) with a field emission gun (FEG) operated at 300 kV and equipped with a TOPS 30 EDX spectrometer (EDAX, Germany).

Solid-state NMR spectroscopy: ¹³C and ⁴ⁱSi MAS solid-state NMR spectra were recorded at ambient temperature on a Bruker Avance III-500 spectrometer in an external magnetic field of 11.74 T, with the samples contained in 4 mm ZrO₂ rotors at spinning frequencies of 10 kHz. The signals were referenced indirectly to 0.1 % TMS in CDCｌ₃. All spectra were acquired using direct excitation, at the Larmor frequencies νCH₃(¹³C) = 125.785 MHz and νCH₃(⁴¹Si) = 99.38 MHz.

UV/Vis spectroscopy: Diffuse reflectance spectra in the range of 240 to 800 nm with 1 nm step size were measured with a Jasco V-650 UV/Vis spectrophotometer equipped with a deuterium and a halogen lamp (Czerny-Turner monochromator with 1200 lines/mm concave grating, photomultiplier tube detector).

Luminescence: Photoluminescence properties of the Eu³⁺- and Ce³⁺-doped samples were measured at room temperature on a HORIBA Fluoromax4 spectrophotometer system, which is connected to an Olympus BX51 microscope by optical fibers. Excitation spectra were acquired with the monitoring wavelength ʎₘₜ₉₉ ranges from 425 to 516 nm. Internal quantum efficiencies (IQEs) were determined by comparing the integrated emission intensities and the absorption at the excitation wavelength with reference materials (BaSO₄, Merck p.a.; commercial (Sr,Ca)Al₂SiN₃:Eu²⁺, Mitsubishi Chemical; and Y₃Al₅O¹₂:Ce³⁺, Philips). Thermal quenching behavior was investigated using an AvaSpec-2048 spectrometer and a stabilized light-emitting diode (LED) light source for sample excitation. A fiber-coupled spectroscopy system containing a thermally stabilized LED light source and a fiber-optic spectrometer (HR2000 + ES spectrometer, Ocean Optics) with the sample placed in an evacuated cooling chamber, equipped with a liquid-He compressor system (ARS4HW, Advanced Research System Inc., Macungie, Pennsylvania, USA) was used for cryo-spectroscopy between 300 and 6 K measured on a thick-bed powder layer.

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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 in the supplementary material of this article.
Keywords: high-temperature chemistry · luminescence · nitridosilicates · NMR spectroscopy · solid-state reactions

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