Supporting information

Influence of composition and structure on the thermal quenching of the 5d-4f emission of Eu²⁺ doped M-Si-N (M = alkali, alkaline earth, rare earth) nitridosilicates

S1 Analysis of the thermal quenching of the luminescence of the Eu²⁺ doped nitridosilicates

In this supporting information, the thermal quenching of the nitridosilicates is analysed for the four categories of thermal quenching mentioned in the main text of the article (see also Fig. 2 of the main article).

S1.1 Thermal quenching according to category 1

First the nitridosilicates will be considered of which the thermal quenching of the emission belongs to category 1. Their emission intensity data approximately follow a linear trend on an $\ln(I_0/I-1)$ vs. $(1/k_BT)$ plot (Fig. 2a of the main article), which means that the thermal quenching behaviour can be well described by:

$$I = \frac{I_0}{1 + C \exp\left(-\frac{E_{act}}{k_B T}\right)}$$
(S1)

Which can be rewritten as:

$$\ln\left(\frac{I_0}{I} - 1\right) = \ln C - E_{act}\left(\frac{1}{k_B T}\right)$$
(S2)

The temperature dependent emission intensity data of these compounds have been fitted according to equation S1 (*I* vs. *T* plot) and according to equation S2 $(\ln(I_0/I-1) \text{ vs. } (1/k_BT) \text{ plot})$ and the obtained fitting parameters are shown in Table S1. Note that, as expected, the activation energy obtained from directly fitting with equation S1 is similar to the activation energy obtained with equation S2. The values of *C* obtained from fitting with equation S1 and S2 show larger relative differences. Nevertheless, the difference is always smaller than one order of magnitude. Note that for Li₂CaSi₂N₄ no reliable fit could be obtained using equation S1, as the standard deviations were too large.

As discussed in section 2.1 of the main article, one of the mechanisms that have been proposed in literature to be responsible for the thermal quenching of the Eu²⁺ 5d-4f emission is a thermally activated non-radiative relaxation via the crossing point of the 5d excited state parabola and the 4f ground state parabola. If this is indeed the main cause of thermal quenching, one may expect a correlation between the Stokes shift and the activation energy for thermal quenching, with a lower activation energy at larger Stokes shift. However, the activation energy does not show a good correlation with the Stokes shift (Fig. S1a). For example, Li₂Ca₂Mg₂Si₂N₆:Eu²⁺ has a very large activation energy of about 0.45 eV and Li₂SrSi₂N₄:Eu²⁺ has a very small activation energy of only 0.13 eV, while both

compounds have the same Stokes shift of 0.36 eV. The weak correlation suggests that direct relaxation to the ground is most probably not the main cause for the thermal quenching. This is in agreement with the work of Dorenbos,¹ who came to the same general conclusion after analysing a large group of inorganic compounds. Note that the small activation energy of BaSi₇N₁₀:Eu²⁺, which also has a large Stokes shift, may initially suggest that there is some correlation. However, the thermal quenching of BaSi₇N₁₀:Eu²⁺ has not been fully determined as the emission is not completely quenched at the highest recorded temperature. It is believed that BaSi₇N₁₀:Eu²⁺ actually has a much larger activation energy for the intrinsic thermal quenching, as is further discussed later on in this supporting information.

Table S1 Overview of the Eu²⁺ doped nitridosilicate phosphors for which the thermal quenching belongs to category 1. Columns 2 and 4 give the activation energy (E_{act}) and constant *C*, respectively, as obtained from directly fitting with equation S1; columns 3 and 5 give E_{act} and *C*, respectively, as obtained from fitting with equation S2; in column 6 the recorded temperature range is given and in column 7 the reference from which the thermal quenching data are obtained.

Equ. S1Equ. S2Equ. S1Equ. S2range (K)LiSi $_2N_3$ *0.230.241.7 * 10 ³ 2.0 * 10 ³ 298-4732SrSiN $_2$ 0.220.223.0 * 10 ² 3.4 * 10 ² 298-4733Sr $_2Si_5N_8$ 0.250.201.2 * 10 ² 3.4 * 10 ¹ 298-5734Sr $_2Si_5N_8$ 0.180.173.9 * 10 ¹ 2.7 * 10 ¹ 5-4335SrSi6N $_8$ 0.260.251.0 * 10 ³ 8.4 * 10 ² 298-5736BaSi ₇ N ₁₀ 0.050.061.3 * 10 ⁰ 3.3 * 10 ¹ 80-4807Sr_8Mg ₇ Si ₉ N ₂₂ 0.080.092.2 * 10 ² 7.3 * 10 ¹ 298-5238Li ₄ Ca ₃ Si ₂ N ₆ 0.440.441.2 * 10 ⁵ 8.9 * 10 ⁴ 298-5239Li ₂ SrSi ₂ N ₄ * \$0.130.121.7 * 10 ² 1.3 * 10 ² 298-47310Li ₂ Ca ₂ Mg ₂ Si ₂ N ₆ \$0.460.433.8 * 10 ⁵ 2.1 * 10 ⁵ 303-56312	Host lattice	E _{act} (eV)	E _{act} (eV)	С	С	Temperature	Reference
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		Equ. S1	Equ. S2	Equ. S1	Equ. S2	range (K)	
SrSiN2 0.22 0.22 $3.0 * 10^2$ $3.4 * 10^2$ 298.473 3 Sr_2Si_5N8 0.25 0.20 $1.2 * 10^2$ $3.4 * 10^1$ 298.573 4 Sr_2Si_5N8 0.18 0.17 $3.9 * 10^1$ $2.7 * 10^1$ 5.433 5 SrSi_6N8 0.26 0.25 $1.0 * 10^3$ $8.4 * 10^2$ 298.573 6 BaSi_7N_{10} 0.05 0.06 $1.3 * 10^0$ $3.3 * 10^1$ 80.480 7 Sr_8Mg_7Si_9N_{22} 0.08 0.09 $2.2 * 10^2$ $7.3 * 10^1$ 298.523 8 Li_4Ca_3Si_2N_6 0.44 0.44 $1.2 * 10^5$ $8.9 * 10^4$ 298.523 9 Li_2SrSi_2N_4 * \$ 0.13 0.12 $1.7 * 10^2$ $1.3 * 10^2$ 298.473 11 Li_2Ca_2Mg_2Si_2N_6 \$ 0.46 0.43 $3.8 * 10^5$ $2.1 * 10^5$ 303.563 12	LiSi ₂ N ₃ *	0.23	0.24	1.7 * 10 ³	2.0 * 10 ³	298-473	2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	SrSiN ₂	0.22	0.22	3.0 * 10 ²	3.4 * 10 ²	298-473	3
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$Sr_2Si_5N_8$	0.25	0.20	1.2 * 10 ²	3.4 * 10 ¹	298-573	4
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$Sr_2Si_5N_8$	0.18	0.17	3.9 * 10 ¹	2.7 * 10 ¹	5-433	5
BaSi ₇ N ₁₀ 0.050.06 1.3×10^{0} 3.3×10^{1} $80-480$ 7Sr_8Mg_7Si_9N_220.080.09 2.2×10^{2} 7.3×10^{1} $298-523$ 8 Li_4Ca_3Si_2N_60.440.44 1.2×10^{5} 8.9×10^{4} $298-523$ 9 Li_2CaSi_2N_4 \times 0.17 2.7×10^{3} $298-423$ 10 Li_2SrSi_2N_4 \times 0.130.12 1.7×10^{2} 1.3×10^{2} $298-473$ 11 Li_2Ca_2Mg_2Si_2N_6 \updownarrow 0.460.43 3.8×10^{5} 2.1×10^{5} $303-563$ 12	SrSi ₆ N ₈	0.26	0.25	$1.0 * 10^3$	8.4 * 10 ²	298-573	6
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$BaSi_7N_{10}$	0.05	0.06	1.3 * 10 ⁰	3.3 * 10 ¹	80-480	7
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$Sr_8Mg_7Si_9N_{22}$	0.08	0.09	2.2 * 10 ²	7.3 * 10 ¹	298-523	8
Li2CaSi2N4 * 0.17 $2.7 * 10^3$ $298-423$ 10 Li2SrSi2N4 * 0.13 0.12 $1.7 * 10^2$ $1.3 * 10^2$ $298-473$ 11 Li2Ca2Mg2Si2N6 0.46 0.43 $3.8 * 10^5$ $2.1 * 10^5$ $303-563$ 12	$Li_4Ca_3Si_2N_6$	0.44	0.44	1.2 * 10 ⁵	8.9 * 10 ⁴	298-523	9
Li2SrSi2N4 * \$ 0.13 0.12 $1.7 * 10^2$ $1.3 * 10^2$ 298-473 11 Li2Ca2Mg2Si2N6 \$ 0.46 0.43 $3.8 * 10^5$ $2.1 * 10^5$ $303-563$ 12	Li ₂ CaSi ₂ N ₄ *		0.17		2.7 * 10 ³	298-423	10
$Li_2Ca_2Mg_2Si_2N_6$ \$ 0.46 0.43 3.8 * 10 ⁵ 2.1 * 10 ⁵ 303-563 ¹²	$Li_2SrSi_2N_4 * $ \$	0.13	0.12	1.7 * 10 ²	1.3 * 10 ²	298-473	11
	$Li_2Ca_2Mg_2Si_2N_6$ \$	0.46	0.43	3.8 * 10 ⁵	2.1 * 10 ⁵	303-563	12
$SrScSi_4N_7$ * 0.28 0.22 3.1×10^3 6.6 $\times 10^2$ 293-453 ¹³	SrScSi ₄ N ₇ *	0.28	0.22	3.1 * 10 ³	6.6 * 10 ²	293-453	13
$SrScSi_4N_7$ * 0.13 0.13 7.1 * 10 ¹ 7.1 * 10 ¹ 298-423 ¹⁴	SrScSi ₄ N ₇ *	0.13	0.13	7.1 * 10 ¹	7.1 * 10 ¹	298-423	14
BaYSi ₄ N ₇ * 0.31 0.31 1.7×10^4 1.7×10^4 298-443 ¹⁵	BaYSi ₄ N ₇ *	0.31	0.31	1.7 * 10 ⁴	1.7 * 10 ⁴	298-443	15

* Thermal quenching is already active at the lowest recorded temperature; as a result the obtained fitting parameters have a relatively high uncertainty.

\$ Data points fluctuate around a straight line.



Fig. S1 The activation energy for thermal quenching (E_{act}) versus a) the Stokes shift (ΔS) of the Eu²⁺ 5d-4f emission and b) $E_{df}^2/(2\Delta S)$ for the Eu²⁺ doped nitridosilicates of thermal quenching category 1. The information about ΔS and E_{df} can be found in our previous publication¹⁶.

One may argue that the activation energy for thermal quenching does not necessarily need to decrease with increasing Stokes shift, even if thermal quenching is caused by a thermally excited cross-over from the 5d to the 4f parabola. The relative positions of the two parabolas and therefore their crossing point are namely also dependent on the absorption and emission energy, which vary among the compounds. However, as discussed in section 2.1 (equation 3) of the main article, if the two parabolas have the same curvature with force constant *k*, the activation energy should be equal to $E_{df}^2/(2\Delta S)$. The activation energy obtained from the fits and presented in Table S1 has been plotted versus $E_{df}^2/(2\Delta S)$ (Fig. S1b). No correlation is observed, but note that the values obtained for $E_{df}^2/(2\Delta S)$ (typically around 6 eV, with the notable exception of $SrSi_6N_{10}:Eu^{2+}$ with direct Si-Si bond) are significantly larger than those obtained for the activation energy (less than 0.6 eV), i.e. more than a factor of 10. This is another indication that direct relaxation to the 4f ground state via the crossing point between the two parabolas cannot be the main cause for thermal quenching.

For Li₂Ca₂Mg₂Si₂N₆:Eu²⁺, Li₄Ca₃Si₂N₆:Eu²⁺ and BaYSi₄N₇:Eu²⁺ the value of *C* (Table S1) obtained by fitting with equation S1 or S2 is relatively large (> 10⁴). However, for the other compounds listed in Table S1, *C* is much smaller and ranges between 1 and 10⁴. *C* is equal to the ratio of the attempt rate for thermal quenching and the radiative decay rate of the 5d-4f emission of Eu²⁺. The first one is typically in the order of 10¹³ s^{-1,1} while the latter one is in the order of 10⁶ s^{-1,1} giving a value of *C* of about 10⁷. Although these rates will vary among the different hosts, it seems not realistic that *C* can be more than a factor 1000 smaller, i.e. smaller than 10⁴.

A possible cause for the lower than expected value of C might be a linear increase of the activation energy with temperature. In order to account for a change of E_{act} with increasing

temperature, we can substitute E_{act} in equation S1 with a linearly temperature-dependent activation energy $E_{act}^*(1+\alpha T)$, where α is a constant:

$$I = \frac{I_0}{1 + C' \exp\left(-\frac{E_{act}(1 + \alpha T)}{k_B T}\right)}$$
(S3)

This equation can be rewritten as:

$$I = \frac{I_0}{1 + C' \exp\left(-\frac{E_{act}}{k_B T}\right) \exp\left(-\frac{E_{act}\alpha}{k_B}\right)} = \frac{I_0}{1 + C \exp\left(-\frac{E_{act}}{k_B T}\right)}$$
(S4)

Hence, the same formula is obtained with a lower value of *C* in case α has a positive value, i.e. if the activation energy increases with increasing temperature. As discussed in section 2.2 of the main article, in case thermal quenching is due to thermal excitation of an electron from the 5d to the conduction band, an increase of the activation energy with increasing temperature is theoretically possible if the increase of the Stokes shift with temperature is larger than the combined effect of a smaller centroid shift, crystal field splitting and bandgap. A complication here is that α and *C'* are not uniquely defined in equation S3 (i.e. a fit has multiple solutions), so for all cases in Table S1 it is possible to obtain a more realistic (i.e. larger) value for *C* as long as one chooses a positive value for α . However, for LiSi₂N₃:Eu²⁺, SrSiN₂:Eu²⁺, Sr₂Si₅N₈:Eu²⁺ and BaSi₇N₁₀:Eu²⁺ the emission band shows a blue shift with increasing temperature and for SrSi₆N₈:Eu²⁺, Li₂CaSi₂N₄:Eu²⁺ and Sr₈Mg₇Si₉N₂₂:Eu²⁺ the emission band does not shift at all with increasing temperature, indicating that the Stokes shift does not increase with increasing temperature, so a positive value of α seems unlikely. For Li₂Ca₂Mg₂Si₂N₆:Eu²⁺ and SrSCSi₄N₇:Eu²⁺ it has not been reported whether the emission bands shift with temperature.

Another possible effect that can be considered when explaining the lower than expected value of *C*, is a possible temperature dependency of the absorption strength. As mentioned before, from a theoretical point of view, equation S1 is defined in terms of the internal quantum efficiency, which is independent of the absorption strength, but the experimental data from literature that has been fitted with this equation are not quantum efficiencies but emission intensities, i.e. also determined by the absorption strength. One can adapt equation S1 in order to account for a linear temperature dependent absorption strength by including a $(1+\beta T)$ term, where β is a constant:

$$I = \frac{I_0(1+\beta T)}{1+C\exp\left(-\frac{E_{act}}{k_B T}\right)}$$
(S5)

Here, β will be negative if the absorption strength decreases with increasing temperature and positive if it increases with temperature. However, the temperature dependent emission data of the phosphors of category 1 cannot be fitted well with the above equation as a non-zero value of β will deviate the graph from a straight line on an $\ln(I_0/I-1)$ vs. $(1/k_BT)$ plot. In addition, non-zero values of β do not significantly increase the value of *C*.

Another mechanism, discussed in section 2.3 of the main article, that should be considered responsible for the low value of C is thermally dependent concentration quenching. This

effect is more pronounced at higher Eu concentrations but cannot be ruled out for the lower concentrated samples (around 1%) considered here, especially if Eu^{2+} ions tend to cluster. A possible way to account for this effect, is to assume that it follows itself also an Arrhenius type of behaviour with its own activation energy and constant *C*. Equation S1 then becomes:

$$I = \frac{I_0}{1 + C_1 \exp\left(-\frac{E_{act1}}{k_B T}\right) + C_2 \exp\left(-\frac{E_{act2}}{k_B T}\right)}$$
(S6)

Here are E_{act1} and C_1 the activation energy and constant C for the intrinsic thermal quenching, respectively, and are E_{act2} and C_2 the activation energy and constant C for the thermally activated concentration quenching, respectively. The results of fitting the thermal quenching data of the compounds of category 1 with equation S6 are shown in Table S2. For $LiSi_2N_3:Eu^{2+}$ and $SrSi_6N_8:Eu^{2+}$, C_1 has now more realistic values well above 10^4 . For $BaYSi_4N_7:Eu^{2+}$, which has already a reasonably high value for C after fitting with equation S1, C_2 and E_{act2} approach zero, removing the second term from the fit. For the other compounds of category 1 that are not shown in Table S2 the fitting parameters could not be obtained with a reasonable amount of accuracy.

Table S2 Results of fitting the compounds of category 1 with equation S6. Activation energies (E_{act1} and E_{act2}), constant C (C_1 and C_2) for each individual term. Column 6 and 7 show the recorded temperature range and reference from which the thermal quenching data are obtained.

Host lattice	E_{act1} (eV)	<i>C</i> ₁	E_{act2} (eV)	<i>C</i> ₂	Range (K)	Ref
LiSi ₂ N ₃	0.46	3.2 * 10 ⁵	0.15	1.7 * 10 ²	298-473	2
$SrSi_6N_8$	0.52	2.0 * 10 ⁵	0.15	4.7 * 10 ¹	298-573	6
BaYSi ₄ N ₇	0.32	7.7 * 10 ⁵	0.01	3.6 * 10 ⁰	298-443	15

Considering that thermally activated concentration quenching may cause additional decrease of emission intensity, it cannot be excluded that for $BaSi_7N_{10}:Eu^{2+}$, this quenching effect is actually the main cause of thermal quenching. The decrease of emission intensity of $BaSi_7N_{10}:2\%Eu^{2+}$ over the recorded temperature range (80 – 480 K) is less than 25%, despite that the intensity already starts to decrease slowly around 100 K. Such a behaviour suggests a quenching process with a low activation energy but with a relatively small probability that is different from the intrinsic thermal quenching observed for the other nitridosilicates.

A final effect that should be considered is the presence of Eu^{2+} in different local environments within one structure. This is for example the case in $Sr_2Si_5N_8$: Eu^{2+} , where there are two types of Sr sites on which Eu^{2+} can substitute. Both sites have a different crystallographic environment and as a consequence one would expect a difference in activation energy for thermal quenching. However, the thermal quenching data discussed above do not consider the luminescence of both sites separately. The emission bands namely strongly overlap, which makes it difficult to consider them individually. Lazarowska et al.¹⁷ studied the effect of the two sites separately by measuring the decay time of the luminescence and found that the activation energies for thermal quenching of Eu at the two sites are 0.34 eV and 0.42 eV. In addition, there is a 0.02 eV activation energy for the non-radiative transfer from one site to the other. The two activation energies are considerably higher than the ones mentioned in Table S1 (0.17 - 0.25 eV). Note that the probabilities for thermal quenching on the two sites obtained by Lazarowska et al. are both, as expected, in the order of 10^9 s^{-1} , while the quenching by the transfer between the sites has a much lower probability in the order of 10^5 s^{-1} . This suggests that the low activation energy and low value of *C* determined from the temperature dependent emission intensity data may be related to the energy transfer between the two sites and an associated energy loss. Also in $\text{Li}_2\text{CaSi}_2\text{N}_4:\text{Eu}^{2+}$ and $\text{Li}_2\text{SrSi}_2\text{N}_4:\text{Eu}^{2+}$ there are two different Sr/Ca sites on which Eu can substitute, while in $\text{Sr}_8\text{Mg}_7\text{Si}_9\text{N}_{22}:\text{Eu}^{2+}$ there are five different Sr sites, but no information on the decay time is available.

S1.2 Thermal quenching according to category 2

The thermal quenching behaviour in α -Si₃N₄:Eu²⁺ and CaYSi₄N₇:Eu²⁺ belongs to category 2: the gradient increases with increasing (1/*k*_B*T*) on an ln(*I*₀/*I*-1) versus (1/*k*_B*T*) plot, i.e. the slope is steeper at lower temperature (Fig. 2b of the main article). Using equation S2, an activation energy can be obtained based on the slope. Since the data are not on a straight line a range of activation energies is obtained based on the variation of slope in different temperature regimes (Table S3).

Table S3 Overview of the Eu^{2+} doped nitridosilicate phosphors for which the thermal quenching behaves according to category 2. Columns 2 and 3 show the activation energy and constant *C* obtained when fitting (using equation S2) the quenching data in the range above the temperature given in column 4. Similarly Columns 5 and 6 show the activation energy and constant *C* obtained when fitting the quenching data in the range below the temperature given in column 7. Column 8 states the reference from which the thermal quenching data have been obtained.

Host lattice	E _{act,} (eV) at high T	C at high T	Temperature (K)	E _{act,max} (eV) at low T	C at low T	Temperature (K)	Ref
α -Si ₃ N ₄	0.11	4.2 * 10 ⁰	> 470 K	0.18	4.2 * 10 ¹	< 400 K	18
$CaYSi_4N_7$	0.07	6.1 * 10 ¹	> 390 K	0.20	3.5 * 10 ³	< 350 K	15

The stronger thermal quenching at lower temperature for α -Si₃N₄:Eu²⁺ and CaYSi₄N₇:Eu²⁺ might be an indication that the activation energy for the thermal quenching decreases with increasing temperature. As discussed above (section S1.1, equation S4), a linear decrease of the activation energy with increasing temperature, will not cause a deviation from a linear behaviour on an $\ln(I_0/I-1)$ versus $(1/k_BT)$ plot, as it will only have an effect on fitting parameter *C* (equation S4). Therefore we assume, as a next least complex behaviour, a quadratic decrease of the activation energy with temperature:

$$I = \frac{I_0}{1 + C \exp\left(-\frac{E_{act}(1 + \alpha T^2)}{k_B T}\right)}$$
(S7)

The temperature dependent emission intensity data of CaYSi₄N₇:Eu²⁺ can be fitted with the above equation. However, the standard error of the fitting parameters is too large in order to draw any meaningful conclusions: e.g. $\alpha = -2 * 10^{-19} \pm 5 * 10^{-8}$ K⁻². For α -Si₃N₄:Eu²⁺ it is impossible to obtain any meaningful fit at all using equation S7. Note that for both CaYSi₄N₇:Eu²⁺ and α -Si₃N₄:Eu²⁺ the thermal quenching data are incomplete. For CaYSi₄N₇:Eu²⁺ there is already significant thermal quenching at the lowest recorded temperature, while for α -Si₃N₄:Eu²⁺ the emission intensity is still relatively strong at the highest recorded temperature (similar as for BaSi₇N₁₀:Eu²⁺).

Instead of a temperature dependency of the activation energy, it may also be the case that the deviations from a straight line on an $\ln(I_0/I-1)$ versus $(1/k_BT)$ plot for the compounds of category 2 are due to an increase of the absorption strength with increasing temperature (i.e. $\beta > 0$ in equation S5). However, just as for fitting with equation S7, a reliable fit cannot be obtained using equation S5 for both α -Si₃N₄:Eu²⁺ and CaYSi₄N₇:Eu²⁺.

Furthermore, it is important to note that the luminescence by both α -Si₃N₄:Eu²⁺ and CaYSi₄N₇:Eu²⁺ is affected by disorder in the structure. In CaYSi₄N₇:Eu²⁺, or actually Ca_{0.8}Y_{1.2}Si₄N_{6.8}C_{0.2}:Eu²⁺, there is disorder due to the presence of some Y at the Ca sites and the replacement of some nitrogen by carbon in the structure, ¹⁹ while in α -Si₃N₄:Eu²⁺, the Eu²⁺ has to create its own site due to the lack of a divalent cation in the lattice. As a result, the Eu²⁺ emission observed in both compounds is a combination of Eu²⁺ emissions from Eu²⁺ in slightly different crystallographic environments. By just considering the temperature dependence of the entire emission band, the effects of the different sites are not taken into account, similarly as was discussed in section S1.1 for Sr₂Si₅N₈:Eu²⁺. Unfortunately, not enough information is available in order to say more about the influence of the individual sites on the thermal quenching.

S1.3 Thermal quenching according to category 3

For the compounds of thermal quenching category 3, the gradient decreases with increasing $(1/k_BT)$ on an $\ln(I_0/I-1)$ versus $(1/k_BT)$ plot, i.e. the slope is steeper at higher temperature (Fig. 2c of the main article). Since the data are not on a straight line, a range of activation energies is obtained, using equation S2 in different temperature regimes, based on the range of slopes (Table S4).

Table S4 Overview of all Eu²⁺ doped nitridosilicate phosphors for which the thermal quenching belongs to category 3. Columns 2 and 3 show the activation energy and constant C obtained when fitting (using equation S2) the quenching data in the range below the temperature given in column 4. Similarly Columns 5 and 6 show the activation energy and constant C obtained when fitting the quenching data the range below the temperature given in column 7. Column 8 states the reference from which the thermal quenching data have been obtained.

Host lattice	<i>E_{act,}</i> (eV)	С	Temperature	<i>E_{act}</i> (eV)	С	Temperature	Ref
	at low T	at low T	(K)	at high T	at high T	(K)	
CaSiN ₂	0.11	7.7 * 10 ¹	< 350 K	0.42	4.1 * 10 ⁶	> 470 K	20
$Ca_{16}Si_{17}N_{34}$	0.17	4.0 * 10 ¹	< 370 K	0.32	1.9 * 10 ³	> 470 K	21
$Ca_2Si_5N_8$	0.11	5.4 * 10 ⁰	< 370 K	0.32	4.7 * 10 ³	> 470 K	4
$BaSi_6N_8$	0.15	1.6 * 10 ¹	< 370 K	0.35	2.8 * 10 ³	> 470 K	22
$SrMg_3SiN_4$	0.02	3.4 * 10 ⁻¹	< 150 K	0.32	5.2 * 10 ⁶	> 260 K	23
$BaMg_3SiN_4$	0.08	6.5 * 10 ⁰	< 300 K	0.36	9.3 * 10 ⁷	> 500 K	24
SrYSi ₄ N ₇	0.15	3.2 * 10 ¹	< 370 K	0.35	7.8 * 10 ³	> 470 K	25
$La_{2.23}Ca_{1.155}Si_6N_{11}$	0.02	3.5 * 10 ⁻¹	< 150 K	0.07	2.4 * 10 ¹	> 200 K	26

Of the compounds of category 3, a special case is the thermal quenching of BaMg₃SiN₄:Eu²⁺. Its emission intensity is constant up to about 150 K, then it starts to decrease slowly, before speeding up above 300 K. At about 550 K all emission is thermally quenched. Bachmann et al.²⁴ ascribed this thermal quenching behaviour to the presence of trapped-exciton emission besides the normal Eu²⁺ 5d-4f emission. This exciton emission can be observed as a sideband at the short wavelength side of the low-temperature emission spectra. The thermal quenching is therefore a combination of two thermal quenching processes: one related to the thermal quenching of exciton emission and the other one related to quenching of the normal Eu²⁺ 5d-4f emission. Using equation S6 the activation energies for the two processes can be obtained, giving 0.08 and 0.46 eV respectively (Table S5). For SrMg₃SiN₄:Eu²⁺ the presence of any trapped-exciton emission is less clear. However, since its thermal quenching behaviour shows a similar pattern as in BaMg₃SiN₄:Eu²⁺ but with a stronger thermal quenching, it might well be that trapped-exciton emission is also present here and affecting the thermal quenching (Table S5).

Table S5 Results of fitting some compounds of category 3 with equation S6. Activation energies (E_{act1} and E_{act2}), constant *C* (C_1 and C_2) for each individual term. In column 6 and 7 the recorded temperature range and reference from which the thermal quenching data are obtained, are shown.

Host lattice	<i>E_{act1}</i> (eV)	<i>C</i> ₁	E _{act2} (eV)	C ₂	Range (K)	Ref
$SrMg_3SiN_4$	0.28	1.1 * 10 ⁶	0.04	4.0 * 10 ⁰	4-310	23
$BaMg_3SiN_4$	0.46	5.7 * 10 ⁵	0.08	6.5 * 10 ⁰	4-600	24

As for the other compounds of category 3, one possibility for the deviation from normal thermal quenching behaviour is a decrease of absorption strength with increasing temperature, i.e. β <0 in equation S5. For some of the compounds of category 3 a meaningful fit can be obtained (Table S6), however only for SrYSi₄N₇:Eu²⁺ a value of *C* is obtained that is relatively large. For CaSiN₂:Eu²⁺ and in particular La_{2.23}Ca_{1.155}Si₆N₁₁:Eu²⁺ the value of *C* is very small. Note that there is no experimental evidence that the absorption strength actually changes with temperature for any of these compounds, neither is there any evidence that it is constant. As for a temperature dependency of the activation energy, a decreasing slope on a ln(*l*₀/*l*-1) versus (1/*k*_B*T*) plot, would require an increasing activation energy with temperature. As discussed before, in case of thermal activation of the 5d electron to the conduction band, an increase of the activation energy would require a significant increase of the Stokes shift with increasing temperature, in order to compensate other effects such as the lowering 4f-5d absorption energy. However, such an increase of the Stokes shift is not observed for the compounds from category 3.

Table S6 Activation energy (E_{act}), the ratio between the rate for thermal quenching and the radiative decay rate of the 5d state of Eu²⁺ (*C*), the temperature at which 50% of the emission is quenched ($T_{50\%}$) and the temperature dependent absorption strength factor (β). Values were obtained by fitting literature data according to equation S5. Columns 5 and 6 show the recorded temperature range and reference from which the thermal quenching data are obtained.

Host lattice	E _{act} (eV)	С	β (K ⁻¹)	Range (K)	Ref
CaSiN ₂	0.22	5.2 * 10 ²	-0.0017	293-573	20
$Ca_{16}Si_{17}N_{34}$	0.43	8.6 * 10 ³	-0.0010	298-523	21
SrYSi ₄ N ₇	0.44	1.9 * 10 ⁴	-0.0013	298-523	25
$La_{2.23}Ca_{1.155}Si_6N_{11}$	0.07	2.1 * 10 ¹	-0.0007	4-300	26

For the compounds of category 3, besides the already discussed $SrMg_3SiN_4:Eu^{2+}$ and $BaMg_3SiN_4:Eu^{2+}$, it cannot be excluded that the deviation from the a normal thermal quenching behaviour is due to a second quenching term, besides the normal intrinsic thermal quenching of the Eu^{2+} 5d-4f emission, e.g. due to anomalous secondary emission like reported for $BaMg_3SiN_4:Eu^{2+}$, or related to thermally activated concentration quenching, as discussed for the compounds of category 1. The results of fitting with equation S6 are shown in Table S7. For compounds that are not listed in Table S7, such a fit could not be obtained with reasonable standard deviations for the fitting variables. For the compounds for which such a fit could be obtained, C_1 has realistic values well above 10^4 , except for $La_{2.23}Ca_{1.155}Si_6N_{11}:Eu^{2+}$, for which C_1 and C_2 are both small.

In $Ca_2Si_5N_8$: Eu^{2+} , $Ca_{16}Si_{17}N_{34}$: Eu^{2+} and $La_{2.23}Ca_{1.155}Si_6N_{11}$: Eu^{2+} , the Eu^{2+} is located at different crystallographic sites. As was discussed in before for $Sr_2Si_5N_8$: Eu^{2+} , this may cause a deviation from the normal thermal quenching behaviour described by equation S1.

E _{act1} (eV)	<i>C</i> ₁	E _{act2} (eV)	<i>C</i> ₂	Temperature range (K)	Ref
0.53	2.5 * 10 ⁶	0.16	1.9 * 10 ²	293-573	20
0.54	1.4 * 10 ⁵	0.13	1.3 * 10 ¹	298-523	21
0.50	1.1 * 10 ⁵	0.16	3.7 * 10 ¹	295-573	4
0.47	1.1 * 10 ⁵	0.05	4.2 * 10 ⁰	298-523	25
0.13	$1.5 * 10^2$	0.04	3.0 * 10 ⁰	4-300	26
	<i>E</i> _{<i>act1</i>} (eV) 0.53 0.54 0.50 0.47 0.13	E_{oct1} (eV) C_1 0.53 $2.5 * 10^6$ 0.54 $1.4 * 10^5$ 0.50 $1.1 * 10^5$ 0.47 $1.1 * 10^5$ 0.13 $1.5 * 10^2$	E_{oct1} (eV) C_1 E_{oct2} (eV)0.53 $2.5 * 10^6$ 0.16 0.54 $1.4 * 10^5$ 0.13 0.50 $1.1 * 10^5$ 0.16 0.47 $1.1 * 10^5$ 0.05 0.13 $1.5 * 10^2$ 0.04	E_{act1} (eV) C_1 E_{act2} (eV) C_2 0.532.5 * 10^60.16 $1.9 * 10^2$ 0.54 $1.4 * 10^5$ 0.13 $1.3 * 10^1$ 0.50 $1.1 * 10^5$ 0.16 $3.7 * 10^1$ 0.47 $1.1 * 10^5$ 0.05 $4.2 * 10^0$ 0.13 $1.5 * 10^2$ 0.04 $3.0 * 10^0$	E_{act1} (eV) C_1 E_{act2} (eV) C_2 Temperature range (K)0.53 $2.5 * 10^6$ 0.16 $1.9 * 10^2$ $293-573$ 0.54 $1.4 * 10^5$ 0.13 $1.3 * 10^1$ $298-523$ 0.50 $1.1 * 10^5$ 0.16 $3.7 * 10^1$ $295-573$ 0.47 $1.1 * 10^5$ 0.05 $4.2 * 10^0$ $298-523$ 0.13 $1.5 * 10^2$ 0.04 $3.0 * 10^0$ $4-300$

Table S7 Activation energies (E_{act1} and E_{act2}), the ratios between the rate for thermal quenching and the radiative decay rate of the 5d state of Eu²⁺ (C_1 and C_2). Values were obtained by fitting literature data according to equation S6. Columns 6 and 7 show the recorded temperature range and reference from which the thermal quenching data are obtained.

S1.4 Thermal quenching according to category 4

The only phosphor belonging to this category is Ba₂Si₅N₈:Eu²⁺, for which Wang et al. reported an increase of the emission intensity with increasing temperature, between 80 and 300 K.²⁷ According to the authors, the increase of emission intensity is due to an (observed) broadening of the emission bands by the increase of the phonon population density and a larger electron-phonon interaction. However, to our opinion, this cannot be the cause of the observed increase of the integrated emission intensity, as a broadening of the emission band goes together with a lowering of the emission maximum. A more likely cause of an increase of integrated emission intensity is a possible increase of absorption strength with increasing temperature. In contrast to what was observed by Wang et al., an increase of emission intensity with increasing temperature was not observed by Piao et al.²⁸ for Ba₂Si₅N₈:Eu²⁺ with the same Eu concentration ($Ba_{1.96}Eu_{0.04}Si_5N_8$). These authors reported a slight decrease of emission intensity with increasing temperature between 4 and 280 K. One possibility for the cause of difference between the two reports, might be a difference in sample preparation, causing a difference in defects or a difference in distribution of Eu²⁺ over the two different crystallographic sites. Above room temperature all authors report a decrease of emission intensity with increasing temperature according to category 1. The fitting results, using equations S1, S2 or S6, are shown in Table S8.

Table S8 Results of fitting the thermal quenching data of $Ba_2Si_5N_8$:Eu²⁺ from various references with equation S1, S2 or S6.

	E_{act} (eV), ref ^{27 a}	E_{act} (eV), ref ²⁹	<i>C</i> , ref ^{27 a}	<i>C</i> , ref ²⁹
Equ. S1	0.50	0.35	3.6 * 10 ⁴	$2.1 * 10^3$
Equ. S2	-	0.26	-	$3.0 * 10^2$
Equ. S6	-	$0.58~(E_{act1}); 0.18~(E_{act2})$	-	$1.8 * 10^{5} (C_{1}); 2.5 * 10^{1} (C_{2})$
a				

^a Using only data above 300 K.

S1.5 Activation energy and quenching temperature

Based on the discussion in the previous sections the activation energy for the intrinsic quenching of the Eu²⁺ 5d-4f emission in the nitridosilicates has been obtained as listed in Table S9. For the compounds of category 1 with a large value of C (> 10^4), i.e. $Li_2Ca_2Mg_2Si_2N_6:Eu^{2+}$, $Li_4Ca_3Si_2N_6:Eu^{2+}$ and $BaYSi_4N_7:Eu^{2+}$, the average activation energy as obtained by fitting with equation S1 and S2 (see Table S1) has been listed. For Sr₂Si₅N₈:Eu²⁺ the activation energies as obtained by Lazarowska et al.¹⁷ have been listed. For BaSi₇N₁₀:Eu²⁺ no activation energy has been listed, because of incomplete thermal quenching data. For the other compounds of category 1 with lower value of C, i.e. LiSi₂N₃:Eu²⁺, SrSiN₂:Eu²⁺, $SrSi_6N_8:Eu^{2+}$, $Sr_8Mg_7Si_9N_{22}:Eu^{2+}$, $Li_2CaSi_2N_4:Eu^{2+}$, $Li_2SrSi_2N_4:Eu^{2+}$ and $SrScSi_4N_7:Eu^{2+}$, the obtained activation energy by fitting with equation S1 or S2 has been listed as a minimum value. For the compounds of category 2 and 4, i.e. α -Si₃N₄:Eu²⁺, CaYSi₄N₇:Eu²⁺ and $Ba_2Si_5N_8:Eu^{2+}$, no activation energy has been listed, due to the uncertainty regarding the thermal guenching in these compounds. Regarding the compounds of category 3, the activation energy has been listed for SrMg₃SiN₄:Eu²⁺ and BaMg₃SiN₄:Eu²⁺, as shown in Table S5.

Compound	E _{act} (eV)	T _{50%} (K)
α -Si ₃ N ₄	?	>600
LiSi ₂ N ₃	>0.23	~420
CaSiN ₂	?	~390
$Ca_{16}Si_{17}N_{34}$?	500
Ca ₂ Si ₅ N ₈	?	460
SrSiN ₂	>0.22	450
Sr ₂ Si ₅ N ₈ (site 1)	0.42	600
$Sr_2Si_5N_8$ (site 2)	0.34	450
SrSi ₆ N ₈	>0.25	440
Ba ₂ Si ₅ N ₈	?	530
BaSi ₇ N ₁₀	?	>600
BaSi ₆ N ₈	?	510
$Sr_8Mg_7Si_9N_{22}$	>0.09	~170
$SrMg_3SiN_4$	0.28	240
BaMg ₃ SiN ₄	0.46	400
$Li_4Ca_3Si_2N_6$	0.44	460
Li ₂ CaSi ₂ N ₄	>0.17	~200
$Li_2SrSi_2N_4$	>0.12	~290
$Li_2Ca_2Mg_2Si_2N_6$	0.45	420
SrScSi ₄ N ₇	>0.22	380
CaYSi ₄ N ₇	?	<300
SrYSi ₄ N ₇	?	460
BaYSi ₄ N ₇	0.31	~370
$La_{2.23}Ca_{1.155}Si_6N_{11}$?	260

Table S9 Activation energy and quenching temperature of the intrinsic thermal quenching in the nitridosilicates.

Also included in Table S9 is the temperature at which 50% of the emission intensity is quenched ($T_{50\%}$), as compared to the intensity at low temperature. $T_{50\%}$ has been obtained directly from the emission intensity versus temperature plots reported in literature, taking into account any thermal quenching that has already occurred at the lowest recorded temperature. In case less than half of the emission intensity has been quenched at the highest recorded temperature (i.e. for α -Si₃N₄:Eu²⁺ and BaSi₇N₁₀:Eu²⁺) only a lower limit for $T_{50\%}$ has been listed.

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