Supplementary information

Dependence of the photoluminescence properties of Eu²⁺ doped M-Si-N (M = alkali, alkaline earth or rare earth) nitridosilicates on their structure and composition

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Relationship between x, y and z in $M_x Si_y N_z$

In this work we have considered all $M_xSi_yN_z$ (M = alkali, alkaline earth or rare earth) nitridosilicate compounds in which Eu^{2+} doping has been reported, including Si_3N_4 itself. Therefore $x \ge 0$, y > 0 and z > 0. Further, there are no limitations for x, y and z other than that the overall compound should be charge neutral, therefore:

 $q_M * x + q_{Si} * y = q_N * z$

Here are q_M , q_{Si} and q_N the absolute values of the charges of M, Si and N respectively. Note that $q_N = 3$ for all compounds, and that $q_{Si} = 4$ for most compounds with the exception of (AE)Si₆N₈ (AE = Sr, Ba) where $q_{Si} = 3.67$ due to the presence of a direct Si-Si bond. In case there are multiple M cations with different charge in one compound, q_M is the weighted average charge of the M cations and x is the total number of M.

$$q_M = \left(x_A + 2x_{AE} + 3x_{RE}\right)/x$$

 $x = x_A + x_{AE} + x_{RE}$

Here are x_A , x_{AE} and x_{RE} the number of alkali (A), alkaline earth (AE) and rare earth (RE) atoms respectively in $A_{xA}AE_{xAE}RE_{xRE}Si_vN_z$.

Linear fits

Table S1: Linear equations and Pearson correlation coefficients (Pearson's r) corresponding to the linear fits through the red data points in the figures of the article. Pearson's r has a value between -1 (perfect negative linear correlation) and +1 (perfect positive linear correlation). A value of 0 indicates no correlation. Note that the fits are used in order to identify and indicate trends in the data and that they do not imply that the actual correlation should be linear.

Figure	Linear equation	Pearson's r
Fig. 2	$E_{\rm fd}({\rm eV}) = (1.5 \pm 0.2) + (1.8 \pm 0.4) \kappa$	0.66
Fig. 3a	$CS(eV) = (2.7 \pm 0.2) - (2.1 \pm 0.3) \kappa$	-0.86
Fig. 4a	$E_{\rm fd}({\rm eV}) = (-3.4 \pm 0.7) + (2.1 \pm 0.3) R_{Eu-N}({\rm \AA})$	0.87
Fig. 4b	$CS(eV) = (4.3 \pm 0.7) - (1.0 \pm 0.2) R_{EU-N}(Å)$	-0.75
Fig. 4c	$CFS(eV) = (8.2 \pm 1.4) - (2.5 \pm 0.5) R_{EU-N}(Å)$	-0.78
Fig. 5	$E_{\rm df}({\rm eV}) = (1.4 \pm 0.1) + (1.3 \pm 0.2) \kappa$	0.67
Fig. 6a	$\Delta S(eV) = (0.1 \pm 0.1) + (0.6 \pm 0.2) \kappa$	0.59
Fig. 6b	T(K) = (-884 ± 231) + (2604 ± 373) κ	0.94
Fig. 7a	$\Delta S(eV) = (-1.4 \pm 0.4) + (0.6 \pm 0.1) R_{Eu-N}(Å)$	0.73
Fig. 7b	$\Delta S(eV) = (-0.4 \pm 0.1) + (0.33 \pm 0.04) E_{fd}(eV)$	0.83
Fig. 7c	$\Delta S(eV) = (-0.3 \pm 0.2) + (0.34 \pm 0.09) E_{df}(eV)$	0.60