**Supporting Information**

# Design of a Nitridoalumosilicate Red Phosphor Synthesized Under Mild Conditions

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## Experiment section

### Materials synthesis

A series of $Ca_{4-4x}SiAl_3N_7$: $xEu^{2+}$ ($0 \leq x \leq 0.005$) samples were synthesized through sample-pressure sintering. Appropriate amounts of $Ca_3N_2$ (Aldrich, >95.0%), AlN (Aldrich, >98.0%), $Si_3N_4$ (Aldrich, 99.5%) and $EuCl_3$ (>99.999%, Aladdin) were weighted and ground in a nitrogen-filled glovebox. The mixture was compressed into an alumina crucible, and then placed into a horizontal tube furnace and annealed at 1350 °C in a $N_2$ atmosphere for four hours. Finally, the furnace-cooled samples were ground into powder for further measurements.

### Measurements and characterizations

The phases of $Ca_{4-4x}SiAl_3N_7$: $xEu^{2+}$ ($0 \leq x \leq 0.005$) were identified by powder X-ray diffraction (PXRD) through a PANalytical X'Pert powder X-ray diffractometer. The Rietveld refinement was carried out using the GSAS program. The morphology of the powder was recorded by a SEM (S-3400, Hitachi, Japan).

The photoluminescence (PL), photoluminescence excitation (PLE) spectra, decay curves, temperature-dependent PL spectra and time-resolved PL (TRPL) spectra of the samples were measured by a FS5 fluorescence spectrometer. The TRPL spectra are constructed by slicing a series of decay curves of the sample obtained by monitoring a continuous wavelength range (500-500 nm, interval of 5 nm). The diffusion reflectance

spectroscopy (DRS) of $Eu^{2+}$-doped and un-doped $Ca_4SiAl_3N_7$ were measured by a Shimadzu UV-2700 spectrophotometer.

The WLEDs were packaged by a SH2012 ultrasonic wire welding machine. The optical performances of the WLEDs were evaluated using a PMS-80 UV-vis-near IR spectrophotocolorimeter.

The bandgap is calculated by the following equations:

$$(\alpha hv)^n = A(hv - E_g) \quad (1)$$

$$\alpha = \frac{(1-R)^2}{2R} \quad (2)$$

Where $\alpha$ is the absorption coefficient, $hv$ is the incident photo energy, $A$ is a constant, and $n$ = 1/2 for indirect bandgap.

The decay curve is well fitted by a two exponential function, which can be expressed by the following equation:

$$I = A_1 exp^{(-t/\tau_1)} + A_2 exp^{(-t/\tau_2)} \quad (3)$$

where $I$ is the emission intensity, $t$ is the time, $A_1$ and $A_2$ are the fitted constants, $\tau_1$ and$\tau_2$ are the lifetime. Thus, the average decay time can be calculated via the following formula:

$$\tau = \frac{\left(A_1\tau_1^2 + A_2\tau_2^2\right)}{\left(A_1\tau_1 + A_2\tau_2\right)} \quad (4)$$

The thermal quenching activation energy ($\Delta E$) of the sample was calculated through the Arrhenius equation: [22]

$$I(T) = I_0/[1 + A\exp(-\Delta E/kT)] \quad (5)$$

Where T represents temperature, I(T) is the emission intensity of the sample at temperature T, $I_0$ is the initial emission intensity, A is the ordinary constant, and K is the Boltzmann constant.

The critical distance (Rc) for $Eu^{2+}$ quenching in $Ca_4SiAl_3N_7$ was calculated based on the following formula：

$$R_c = 2[\frac{3V}{4\pi N x_c}]^{\frac{1}{3}} \quad (6)$$

where $x_c$ is the optimal $Eu^{2+}$ doping concentration, V is the unit cell volume, and N is the number of $Ca^{2+}$ atoms in a single unit cell.

Table S1 Crystal structure information of several silicon-based nitrides

| Phase | Si/（Al+Si） | Smallest structural unit | Basic structural unit | Connection type | Ref. |
|---|---|---|---|---|---|
| $Sr_2Si_5N_8$ | 1 | $SiN_4$ | $Si_6N_{18}$ six-membered ring | common angle, common edge | [23] |
| $CaSiN_2$ | 1 | $SiN_4$ | $Si_6N_{18}$ six-membered ring | common angle, common edge | [24] |
| $Ba_2AlSi_5N_9$ | 5/6 | $SiN_4$、$AlN_4$ | $Si(Al)_6N_{18}$ six-membered ring | common angle, common edge | [25] |
| $SrAlSi_4N_7$ | 4/5 | $SiN_4$、$AlN_4$ | $Si_6AlN_{21}$ seven-membered ring | $AlN_4$-common edge、$SiN_4$-common angle | [26] |
| $CaAlSiN_3$ | 1/2 | $SiN_4$、$AlN_4$ | $Si(Al)_6N_{18}$ six-membered ring | common angle | [19] |
| $Ca_5Si_2Al_2N_8$ | 1/2 | $SiN_4$、$AlN_4$ | $Al_6N_{18}$ six-membered ring | $AlN_4$- common angle, common edge、$SiN_4$- common edge | [27] |
| $Ca_4SiAl_3N_7$ | 1/4 | $SiN_4$、$AlN_4$ | $Al_4SiN_{15}$ five-membered ring | $AlN_4$- common angle, common edge、$SiN_4$- common edge | This work |

Table S2 crystallographic data of $Ca_4SiAl_3N_7$

| |
|---|
| Formula sum: $Ca_4SiAl_3N_7$ |
| Formula weight: 1101.06 g/mol |
| Crystal system: triclinic |
| Space-group: P -1 (2) |
| Cell parameters: a=5.8778 Å, b=8.1422 Å, c=13.0503 Å, α=78.2130°, β=76.8350° γ=82.3320°, |
| Cell ratio: a/b=0.7219 b/c=0.6239 c/a=2.2203 |
| Cell volume: 592.85 $Å^3$ |

Calc. density: 3.08385 g/cm$^3$

Formula type: N2O10P12Q21

Wyckoff sequence: i22a

Table S3 Atomic parameters of $Ca_4SiAl_3N_7$

| Atom | Wyck. | x/a | y/b | z/c |
|---|---|---|---|---|
| Ca1 | 2i | 0.0949 | 0.0433 | 0.6526 |
| Ca2 | 2i | 0.1163 | 0.2899 | 0.9860 |
| Ca3 | 2i | 0.2950 | 0.4018 | 0.4618 |
| Ca4 | 2i | 0.5011 | 0.2567 | 0.7110 |
| Ca5 | 2i | 0.6021 | 0.0664 | 0.0976 |
| Ca6 | 2i | 0.7594 | 0.3465 | 0.2192 |
| Si1 | 2i | 0.1191 | 0.9249 | 0.1246 |
| Al1 | 2i | 0.0050 | 0.5976 | 0.3023 |
| Al2 | 2i | 0.1797 | 0.7246 | 0.5312 |
| Al3 | 2i | 0.2508 | 0.2268 | 0.2574 |
| Al4 | 2i | 0.3939 | 0.5721 | 0.0854 |
| Al5 | 2i | 0.3990 | 0.0638 | 0.4183 |
| N1 | 2i | 0.0960 | 0.2164 | 0.7917 |
| N2 | 2i | 0.1016 | 0.1681 | 0.4041 |
| N3 | 2i | 0.1166 | 0.6800 | 0.4044 |
| N4 | 2i | 0.1295 | 0.1217 | 0.1722 |
| N5 | 2i | 0.2399 | 0.4615 | 0.2229 |
| N6 | 2i | 0.2638 | 0.5208 | 0.6263 |
| N7 | 2i | 0.4182 | 0.8042 | 0.0940 |
| N8 | 2i | 0.5419 | 0.1111 | 0.2769 |
| N9 | 2i | 0.5474 | 0.1559 | 0.5092 |
| N10 | 2i | 0.7052 | 0.4473 | 0.0425 |
| N11 | 1a | 0 | 0 | 0 |

Table S4 The bond length data of Ca-N bond

| type | bond length (Å) | type | bond length (Å) | type | bond length (Å) |
|---|---|---|---|---|---|
| Ca1-N1 | 2.517(2) | Ca2-N1 | 2.735(1) | Ca3-N2 | 2.652(4) |
| Ca1-N2 | 2.507(3) | Ca2-N4 | 2.545(3) | Ca3-N3 | 2.413(2) |
| Ca1-N3 | 2.483(5) | Ca2-N7 | 2.749(3) | Ca3-N3 | 2.728(4) |
| Ca1-N4 | 2.573(4) | Ca2-N10 | 2.432(2) | Ca3-N6 | 2.494 (1) |
| Ca1-N8 | 2.564(1) | Ca2-N10 | 2.595(5) | Ca3-N6 | 2.688 (2) |
| Ca1-N9 | 3.016(2) | Ca2-N11 | 2.504(5) | Ca3-N9 | 2.390 (3) |
| | | | | | |
| Ca4-N1 | 2.411(2) | Ca5-N1 | 3.017(6) | Ca6-N4 | 2.864(5) |
| Ca4-N3 | 2.456(5) | Ca5-N4 | 2.735(4) | Ca6-N5 | 3.065(5) |
| Ca4-N6 | 2.593(5) | Ca5-N7 | 2.530(4) | Ca6-N5 | 3.097(6) |
| Ca4-N7 | 2.636(3) | Ca5-N7 | 2.550(4) | Ca6-N6 | 2.445(3) |
| Ca4-N8 | 2.999(1) | Ca5-N8 | 2.381(2) | Ca6-N8 | 2.345(4) |
| Ca4-N9 | 2.860(1) | Ca5-N11 | 2.443(3) | Ca6-N10 | 2.363(4) |
| | | | | | |
| Average | 2.617 | | | | |

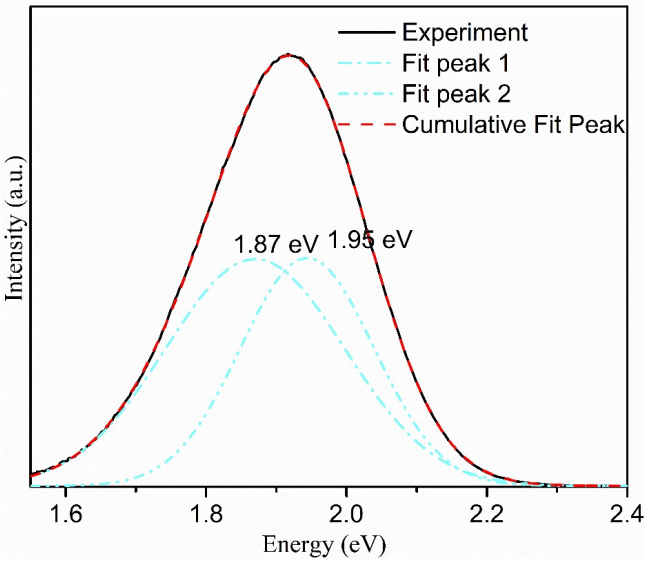


Fig. S1 Gauss Fit of the emission of $Ca_4SiAl_3N_7:Eu^{2+}$.

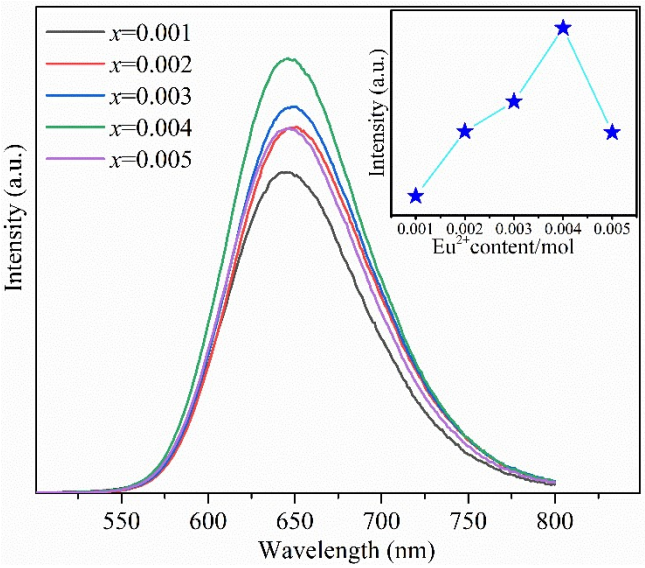


Fig. S2 Emission spectra of $Ca_{4-4x}SiAl_3N_7$: $xEu^{2+}$ ($0 \leq x \leq 0.005$).

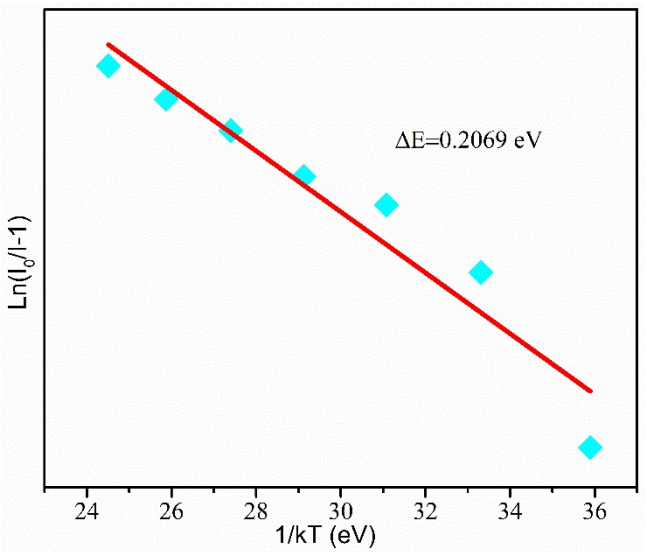


Fig. S3 Relationship between Ln ($I_0$/I-1) and 1/KT.

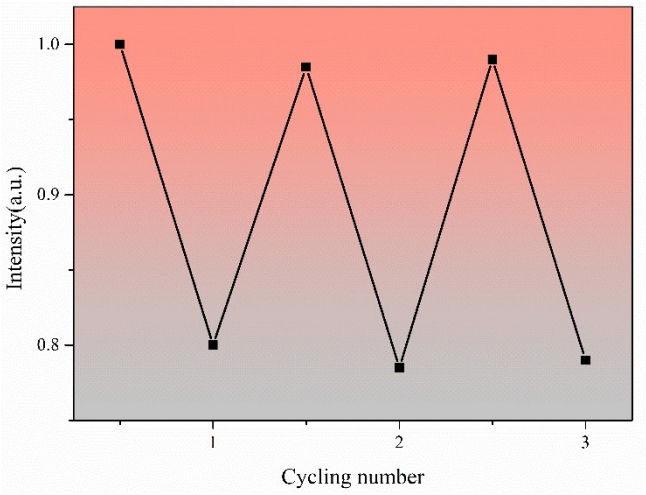


Fig. S4 Dependent of emission intensity on thermal quenching cycle between 298 and 473 K.