Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Crystal structure, tunable emission and applications of $Ca_{1-x}Al_{1-x}Si_{1+x}N_{3-x}O_x$: RE ($x$ = 0-0.22, RE = Eu^{2+}, Ce^{3+}) solid solution phosphors for white light-emitting diodes

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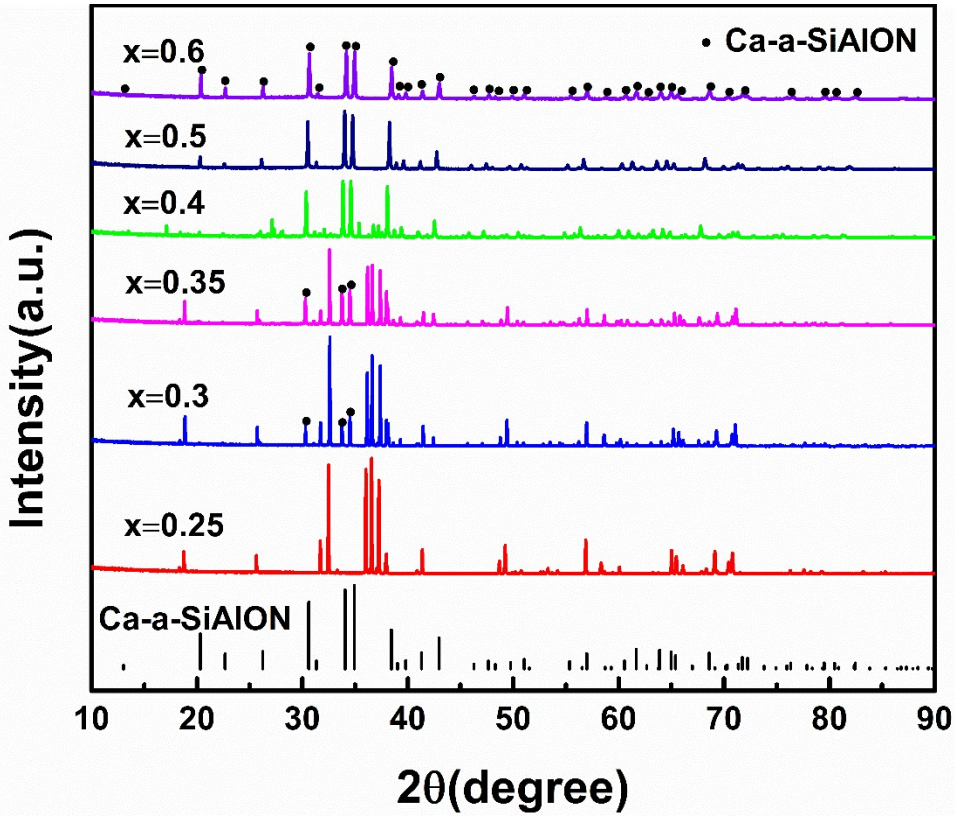

Fig. S1 XRD patterns of samples of $Ca_{1-x}Al_{1-x}Si_{1+x}N_{3-x}O_x$ (x = 0.25, 0.3, 0.35, 0.4, 0.5, 0.6).

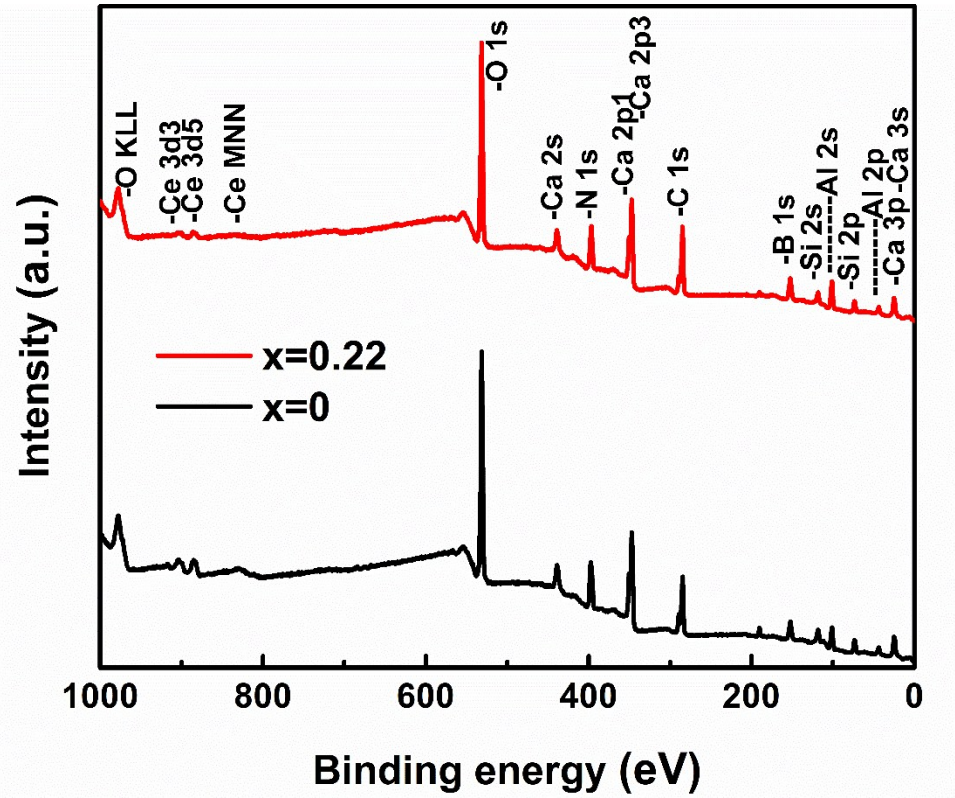

Fig. S2 XPS survey scan for the samples of $Ca_{1-x}Al_{1-x}Si_{1+x}N_{3-x}O_x$:Ce 1% ($x$ = 0 and 0.22).

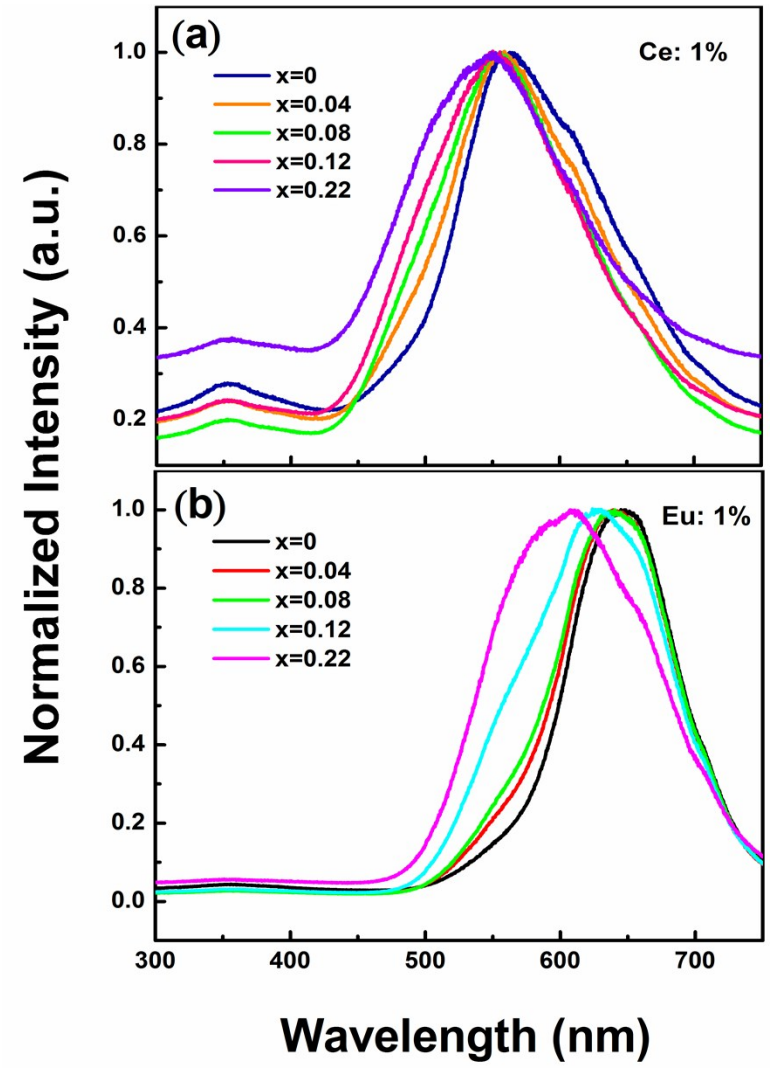

Fig. S3 Cathodoluminescence spectra of (a) $Ca_{1-x}Al_{1-x}Si_{1+x}N_{3-x}O_x$:Ce 1% and (b) $Ca_{1-x}Al_{1-x}Si_{1+x}N_{3-x}O_x$:Eu 1%.

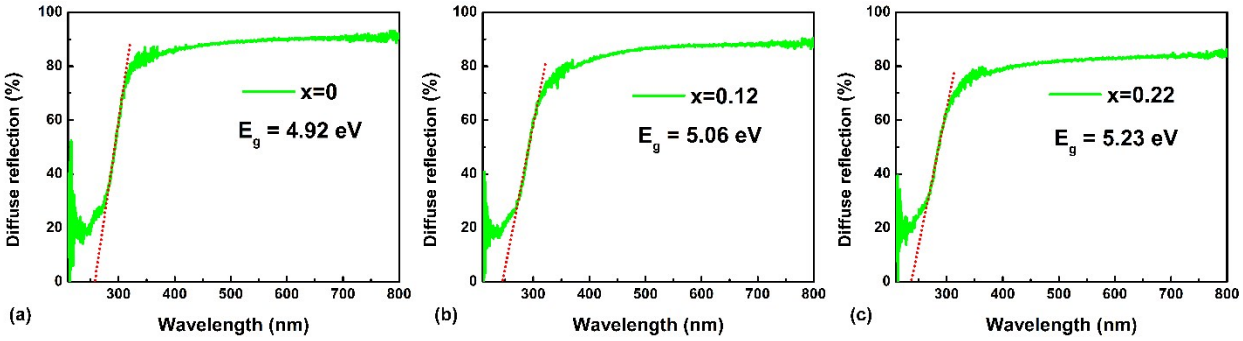

Fig. S4 Diffusion reflection spectra of $Ca_{1-x}Al_{1-x}Si_{1+x}N_{3-x}O_x$ with (a) $x = 0$, (b) $x = 0.12$, and (c) $x = 0.22$.

Table S1 Analyzed cationic ratios of $Ca_{1-x}Al_{1-x}Si_{1+x}N_{3-x}O_x$ (x = 0, 0.04, 0.08, 0.12, 0.22)

Sample	Initial composition			Final composition[a]		
	Ca	Al	Si	Ca	Al	Si
x = 0	1	1	1	0.96	1.02	0.98
x = 0.04	0.96	0.96	1.04	0.94	0.98	1.02
x = 0.08	0.92	0.92	1.08	0.92	0.94	1.06
x = 0.12	0.88	0.88	1.12	0.87	0.89	1.11
x = 0.22	0.78	0.78	1.22	0.78	0.78	1.22

[a]Normalized against the total Al + Si = 2.

Table S2 Analyzed N/O ratios of $Ca_{1-x}Al_{1-x}Si_{1+x}N_{3-x}O_x$ (x = 0, 0.04, 0.08, 0.12, 0.22)

Sample	Initial composition		Final composition[b]	
	N	O	N	O
x = 0	3	0	2.91	0.09
x = 0.04	2.96	0.04	2.87	0.13
x = 0.08	2.92	0.08	2.84	0.16
x = 0.12	2.88	0.12	2.82	0.18
x = 0.22	2.78	0.22	2.78	0.22

[b]Normalized against the total N + O = 3.

Table S3 Atomic coordination of $Ca_{1-x}Al_{1-x}Si_{1+x}N_{3-x}O_x$ (x = 0)

Atom	x	y	z	Occupancy	Uiso
Ca1	0	0.3151(9)	0.4950(2)	1.00	0.0150(3)
(Si/Al)1	0.1740(3)	0.1582(9)	0.0208(4)	0.50/0.50	0.0068(7)
N1	0.2127(1)	0.1219(7)	0.3749(9)	1.00	0.0015(0)
N2	0	0.2454(7)	-0.0173(1)	1.00	0.0049(5)

Table S4 Atomic coordination of $Ca_{1-x}Al_{1-x}Si_{1+x}N_{3-x}O_x$ (x = 0.12)

Atom	x	y	z	Occupancy	Uiso
Ca1	0	0.3259(3)	0.4951(9)	1.00	0.0184(9)
(Si/Al)1	0.1747(4)	0.1545(7)	0.0215(2)	0.44/0.56	0.0058(2)
(N/O)1	0.2143(4)	0.1275(6)	0.3755(6)	1.00	0.0004(0)
(N/O)2	0	0.2374(4)	-0.0181(6)	1.00	0.0065(5)

Table S5 Atomic coordination of $Ca_{1-x}Al_{1-x}Si_{1+x}N_{3-x}O_x$ (x = 0.22)

Atom	x	y	z	Occupancy	Uiso
$(Ca/V_{Ca})1$	0.6916(6)	0.8357(6)	0.2690(8)	0.78/0.22	0.0231(3)
Si1	0.3593(9)	0.1479(0)	-0.2017(1)	1.00	0.0040(2)
(Si/Al)2	0.5095(4)	0.3438(2)	0.2985(2)	0.22/0.78	0.0109(0)
(N/O)1	0.4608(0)	0.6353(6)	0.1615(1)	1.00	0.0037(0)
(N/O)2	0.3899(8)	0.1226(2)	0.1478(2)	1.00	0.0017(6)
(N/O)3	0.6972(8)	0.2625(4)	0.2725(2)	1.00	0.0138(2)

Table S6 Selected bond length (Å) of $Ca_{1-x}Al_{1-x}Si_{1+x}N_{3-x}O_x$ (x = 0)

Ca1-N1	2.4284(25)	(Si/Al)1-N1	1.8432(24)
Ca1-N1	2.4284(25)	(Si/Al)1-N1	1.7875(32)
Ca1-N2	2.622(4)	(Si/Al)1-N1	1.8208(31)
Ca1-N2	2.499(4)	(Si/Al)1-N2	1.7841(14)
Ca1-N2	2.4829(33)		
Average	2.4923(17)	Average	1.8089(25)

Table S7 Selected bond length (Å) of $Ca_{1-x}Al_{1-x}Si_{1+x}N_{3-x}O_x$ (x = 0.12)

Ca1-(N/O)1	2.4364(26)	(Si/Al)1-(N/O)1	1.8315(28)
Ca1-(N/O)1	2.4364(26)	(Si/Al)1-(N/O)1	1.7974(26)
Ca1-(N/O)2	2.636(5)	(Si/Al)1-(N/O)1	1.7928(27)
Ca1-(N/O)2	2.503(5)	(Si/Al)1-(N/O)2	1.7689(15)
Ca1-(N/O)2	2.468(4)		
Average	2.4962(50)	Average	1.7976(74)

Table S8 Selected bond length (Å) of $Ca_{1-x}Al_{1-x}Si_{1+x}N_{3-x}O_x$ (x = 0.22)

Ca1-(N/O)1	2.547(7)	Si1-(N/O)1	1.709(7)
Ca1-(N/O)2	2.333(7)	Si1-(N/O)2	1.785(7)
Ca1-(N/O)3	2.413(5)	Si1-(N/O)2	1.731(7)
Ca1-(N/O)3	2.555(7)	Si1-(N/O)3	1.642(9)
Ca1-(N/O)3	2.589(7)	(Si/Al)2-(N/O)1	1.846(7)
		(Si/Al)2-(N/O)1	1.885(7)
		(Si/Al)2-(N/O)2	1.859(7)
		(Si/Al)2-(N/O)3	1.864(9)
Average	2.488(1)	Average	1.790(9)