Photoluminescence Tuning *via* Cation Substitution in Oxonitridosilicate Phosphors: DFT Calculations, Different Site Occupations, and Luminescence Mechanisms

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Table S1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	B_{iso}*/B_{eq}
Ba1	0	0.2707	0.0209	0.1 (6)
Ba2	0.517 (5)	0.709 (5)	-0.0157 (18)	0.1 (6)
Ba3	0.495 (6)	0.225 (3)	0.531 (2)	0.1 (5)
Sr	-0.004 (5)	0.750 (5)	0.4810 (18)	0.1 (4)
Si1_1	0.527 (3)	0.480 (2)	0.2144 (10)	0.10 (12)
Si1_2	0.024 (3)	0.591 (3)	0.7961 (12)	0.10 (12)
Si1_3	0.005 (3)	0.076 (3)	0.7017 (10)	0.10 (12)
Si1_4	0.516 (3)	0.999 (3)	0.3016 (11)	0.10 (12)
Si2_1	0.547 (3)	0.265 (3)	0.7970 (11)	0.10 (12)
Si2_2	0.046 (3)	0.716 (4)	0.2108 (12)	0.10 (12)
Si2_3	0.053 (3)	0.236 (4)	0.3094 (11)	0.10 (12)
Si2_4	0.542 (3)	0.770 (3)	0.6892 (11)	0.10 (12)
O1_1	0.456 (4)	0.381 (3)	0.1060 (12)	0.10 (12)
O1_2	-0.008 (4)	0.702 (5)	0.9051 (15)	0.10 (12)
O1_3	-0.048 (3)	0.118 (5)	0.5895 (14)	0.10 (12)
O1_4	0.485 (4)	0.903 (3)	0.4125 (13)	0.10 (12)
N1_1	0.882 (4)	0.460 (3)	0.2304 (12)	0.10 (7)
N1_2	0.379 (4)	0.559 (3)	0.7691 (10)	0.10 (7)
N1_3	0.367 (3)	0.047 (3)	0.7208 (10)	0.10 (7)
N1_4	0.874 (3)	0.972 (3)	0.2634 (11)	0.10 (7)
N2_1	0.388 (4)	0.769 (3)	0.2274 (9)	0.10 (7)
N2_2	0.879 (4)	0.298 (3)	0.7800 (11)	0.10 (7)
N2_3	0.884 (3)	0.789 (3)	0.7183 (12)	0.10 (7)
N2_4	0.390 (3)	0.279 (3)	0.2909 (10)	0.10 (7)
O2_1	0.527 (4)	0.674 (3)	0.5807 (14)	0.10 (12)
O2_2	-0.005 (4)	0.277 (6)	0.4214 (14)	0.10 (12)
O2_3	-0.041 (4)	0.793 (5)	0.1028 (16)	0.10 (12)
O2_4	0.504 (4)	0.185 (3)	0.9086 (14)	0.10 (12)

Symmetry codes: (i) *x*-1, *y*, *z*; (ii) *x*, *y*, *z*-1; (iii) *x*, *y*-1, *z*; (iv) *x*-1, *y*, *z*-1; (v) *x*+1, *y*, *z*-1; (vi) *x*+1, *y*, *z*; (vii) *x*, *y*+1, *z*-1; (viii) *x*, *y*+1, *z*; (ix) *x*-1, *y*-1, *z*.

Table S2. Geometric parameters (Å, º)

Ba1—O1_1	2.577	Si1_2—O1_2	1.68 (3)
Ba1—O1_1^{i}	2.940	Si1_2—N1_2	1.76 (2)
Ba1—O1_2^{ii}	2.880	Si1_2—N2_2^{i}	1.76 (2)
Ba1—O2_3^{iii}	2.868	Si1_2—N2_3^{i}	1.69 (2)
Ba1—O2_4^{ii}	2.937	Si1_3—O1_3	1.64 (3)
Ba1—O2_4^{iv}	2.912	Si1_3—N1_3	1.77 (2)
Ba2—O1_1	2.51 (3)	Si1_3—N2_2^{i}	1.76 (2)
Ba2—O1_2^{ii}	2.77 (3)	Si1_3—N2_3^{ix}	1.69 (2)
Ba2—O1_2^{v}	2.54 (3)	Si1_4—O1_4	1.68 (2)
Ba2—O2_3^{vi}	2.76 (3)	Si1_4—N1_4	1.81 (2)
Ba2—O2_4^{vii}	2.82 (3)	Si1_4—N2_1	1.76 (2)
Ba3—O1_3	2.79 (3)	Si1_4—N2_4^{viii}	1.65 (2)
Ba3—O1_3^{vi}	2.42 (3)	Si2_1—N1_2	1.84 (2)
Ba3—O1_4^{iii}	2.44 (3)	Si2_1—N1_3	1.84 (2)
Ba3—N1_3	2.95 (3)	Si2_1—N2_2	1.62 (2)
Ba3—O2_1	2.56 (3)	Si2_1—O2_4	1.67 (3)
Ba3—O2_2	2.88 (4)	Si2_2—N1_1^{i}	1.63 (3)
Ba3—O2_2^{vi}	2.88 (4)	Si2_2—N1_4^{i}	1.79 (2)
Sr—O1_3^{viii}	2.55 (3)	Si2_2—N2_1	1.69 (2)
Sr—O1_4	2.68 (3)	Si2_2—O2_3	1.65 (3)
Sr—O1_4^{i}	2.77 (3)	Si2_3—N1_1^{i}	1.86 (2)
Sr—O2_1	2.95 (3)	Si2_3—N1_4^{ix}	1.81 (2)
Sr—O2_1^{i}	2.69 (3)	Si2_3—N2_4	1.65 (2)
Sr—O2_2	2.72 (4)	Si2_3—O2_2	1.64 (3)
Si1_1—O1_1	1.68 (2)	Si2_4—N1_2	1.80 (2)
Si1_1—N1_1	1.72 (2)	Si2_4—N1_3^{viii}	1.79 (2)
Si1_1—N2_1	1.725 (19)	Si2_4—N2_3	1.70 (2)
Si1_1—N2_4	1.68 (2)	Si2_4—O2_1	1.64 (3)
O1_1—Ba1—O1_1^{i}	120.7 (11)	O2_1^{i}—Sr—O2_2	91.1 (9)
O1_1—Ba1—O1_2^{ii}	95.3 (6)	O1_1—Si1_1—N1_1	107.7 (12)
O1_1—Ba1—O2_3^{iii}	94.5 (6)	O1_1—Si1_1—N2_1	108.6 (11)

O1_1—Ba1—O2_4^{ii}	66.3 (9)	O1_1—Si1_1—N2_4	107.9 (11)
O1_1^{i}—Ba1—O1_2^{ii}	93.3 (5)	N1_1—Si1_1—N2_1	115.1 (13)
O1_1^{i}—Ba1—O2_3^{iii}	87.6 (5)	N1_1—Si1_1—N2_4	105.1 (11)
O1_1^{i}—Ba1—O2_4^{iv}	62.4 (10)	N2_1—Si1_1—N2_4	112.2 (12)
O1_2^{ii}—Ba1—O2_4^{ii}	80.2 (6)	O1_2—Si1_2—N1_2	109.1 (13)
O1_2^{ii}—Ba1—O2_4^{iv}	78.7 (6)	O1_2—Si1_2—N2_2^{i}	114.6 (16)
O2_3^{iii}—Ba1—O2_4^{ii}	97.6 (6)	O1_2—Si1_2—N2_3^{i}	109.9 (15)
O2_3^{iii}—Ba1—O2_4^{iv}	91.3 (5)	N1_2—Si1_2—N2_2^{i}	105.3 (12)
O2_4^{ii}—Ba1—O2_4^{iv}	110.2 (8)	N1_2—Si1_2—N2_3^{i}	107.8 (12)
O1_1—Ba2—O1_2^{ii}	99.7 (11)	N2_2^{i}—Si1_2—N2_3^{i}	109.7 (12)
O1_1—Ba2—O1_2^{v}	113.6 (15)	O1_3—Si1_3—N1_3	108.5 (12)
O1_1—Ba2—O2_3^{vi}	77.5 (13)	O1_3—Si1_3—N2_2^{i}	118.2 (16)
O1_2^{ii}—Ba2—O1_2^{v}	129 (2)	O1_3—Si1_3—N2_3^{ix}	102.3 (13)
O1_2^{ii}—Ba2—O2_4^{vii}	80.4 (11)	N1_3—Si1_3—N2_2^{i}	107.4 (11)
O1_2^{v}—Ba2—O2_3^{vi}	65.6 (17)	N1_3—Si1_3—N2_3^{ix}	103.5 (11)
O1_2^{v}—Ba2—O2_4^{vii}	82.2 (11)	N2_2^{i}—Si1_3—N2_3^{ix}	115.9 (14)
O2_3^{vi}—Ba2—O2_4^{vii}	95.7 (10)	O1_4—Si1_4—N1_4	109.9 (13)
O1_3—Ba3—O1_3^{vi}	134 (3)	O1_4—Si1_4—N2_1	108.5 (12)
O1_3—Ba3—O1_4^{iii}	92.3 (10)	O1_4—Si1_4—N2_4^{viii}	110.2 (13)
O1_3—Ba3—N1_3	57.5 (7)	N1_4—Si1_4—N2_1	95.1 (10)
O1_3—Ba3—O2_1	100.1 (11)	N1_4—Si1_4—N2_4^{viii}	113.4 (13)
O1_3—Ba3—O2_2	53.6 (8)	N2_1—Si1_4—N2_4^{viii}	118.8 (14)
O1_3^{vi}—Ba3—O1_4^{iii}	94.9 (11)	N1_2—Si2_1—N1_3	103.4 (10)
O1_3^{vi}—Ba3—N1_3	77.8 (12)	N1_2—Si2_1—N2_2	107.4 (11)
O1_3^{vi}—Ba3—O2_1	94.4 (11)	N1_2—Si2_1—O2_4	112.4 (13)
O1_3^{vi}—Ba3—O2_2^{vi}	57 (2)	N1_3—Si2_1—N2_2	116.7 (13)
O1_4^{iii}—Ba3—N1_3	113.4 (13)	N1_3—Si2_1—O2_4	109.9 (12)
O1_4^{iii}—Ba3—O2_1	152 (5)	N2_2—Si2_1—O2_4	107.1 (12)
O1_4^{iii}—Ba3—O2_2	71.3 (16)	N1_1^{i}—Si2_2—N1_4^{i}	112.2 (13)
O1_4^{iii}—Ba3—O2_2^{vi}	73.2 (15)	N1_1^{i}—Si2_2—N2_1	126.5 (19)
N1_3—Ba3—O2_1	94.0 (10)	N1_1^{i}—Si2_2—O2_3	104.9 (15)
N1_3—Ba3—O2_2	111.2 (14)	N1_4^{i}—Si2_2—N2_1	104.7 (12)

N1_3—Ba3—O2_2^{vi}	135 (3)	N1_4^{i}—Si2_2—O2_3	94.5 (14)
O2_1—Ba3—O2_2	96.3 (11)	N2_1—Si2_2—O2_3	109.5 (13)
O2_1—Ba3—O2_2^{vi}	90.3 (10)	N1_1^{i}—Si2_3—N1_4^{ix}	95.4 (10)
O2_2—Ba3—O2_2^{vi}	113.1 (15)	N1_1^{i}—Si2_3—N2_4	104.1 (12)
O1_3^{viii}—Sr—O1_4	92.7 (9)	N1_1^{i}—Si2_3—O2_2	115.2 (17)
O1_3^{viii}—Sr—O1_4^{i}	84.5 (10)	N1_4^{ix}—Si2_3—N2_4	121.5 (16)
O1_3^{viii}—Sr—O2_1	83.5 (10)	N1_4^{ix}—Si2_3—O2_2	112.7 (16)
O1_3^{viii}—Sr—O2_1^{i}	74.4 (13)	N2_4—Si2_3—O2_2	107.5 (13)
O1_4—Sr—O1_4^{i}	124 (2)	N1_2—Si2_4—N1_3^{viii}	100.4 (10)
O1_4—Sr—O2_1	57.5 (7)	N1_2—Si2_4—N2_3	107.6 (11)
O1_4—Sr—O2_2	100.6 (11)	N1_2—Si2_4—O2_1	111.8 (12)
O1_4^{i}—Sr—O2_1^{i}	59.7 (19)	N1_3^{viii}—Si2_4—N2_3	109.9 (11)
O1_4^{i}—Sr—O2_2	100.1 (10)	N1_3^{viii}—Si2_4—O2_1	119.4 (14)
O2_1—Sr—O2_1^{i}	116.4 (15)	N2_3—Si2_4—O2_1	107.2 (12)
O2_1—Sr—O2_2	91.1 (9)		

Table S3. Calculated structural data of Phase 1

	x/a	*y/b*	*z/c*
Sr1	0.16205(0.175)	0.11757(0.123)	0.06584(0.068)
Sr2	0.63763(0.631)	0.23044(0.225)	0.31687(0.3227)
Sr3	0.15221(0.178)	0.10763(0.104)	-0.44144(-0.4271)
Sr4	0.62659(0.631)	0.22036(0.221)	0.81081(0.8217)
Si1_1	0.47143(0.4751)	-0.22359(-0.2101)	-0.25805(-0.1774)
Si1_2	0.36429(0.3651)	-0.43586(0.5713)	0.08239(0.0771)
Si1_3	-0.22558(-0.2224)	0.57013(0.5642)	-0.00495(-0.0027)
Si1_4	0.97707(0.9769)	-0.23163(-0.2426)	0.24901(0.2454)
Si2_1	0.05952(0.0615)	-0.22826(-0.2276)	0.83276(0.8310)
Si2_2	0.55626(0.5462)	-0.2228(-0.2240)	0.33109(0.3338)
Si2_3	0.27716(0.2818)	-0.43948(-0.4426)	0.49631(0.5050)
Si2_4	0.85624(0.8578)	0.56606(0.5625)	0.58145(0.5816)
O1_1	0.37965(0.3229)	0.33772(0.3637)	0.07309(0.0701)
O1_2	0.40879(0.4427)	-0.00207(0.0143)	0.80388(0.7784)
O1_3	0.95811(0.9677)	-0.01409(-0.0402)	0.31549(0.3373)
O1_4	-0.17195(-0.1766)	0.3484(0.3596)	0.05634(0.0968)
O2_1	-0.04036(-0.0228)	-0.00208(-0.0180)	0.82723(0.7513)
O2_2	0.42379(0.4330)	-0.00807(-0.0033)	0.31301(0.3499)
O2_3	0.82993(0.8311)	0.34986(0.3499)	0.56764(0.5574)
O2_4	0.36379(0.3362)	-0.65541(-0.6671)	0.56401(0.5465)
N1_1	0.54053(0.5445)	-0.38439(-0.3740)	0.91903(0.9196)
N1_2	0.64071(0.6393)	-0.26539(-0.2711)	0.55013(0.5485)
N1_3	0.1441(0.1450)	-0.27842(-0.2636)	0.05235(0.0508)
N1_4	0.04368(0.0484)	-0.39791(-0.3953)	-0.57659(-0.5709)
N2_1	0.91695(0.9173)	-0.38422(-0.3864)	0.80038(0.8000)
N2_2	0.76359(0.757)	-0.27026(-0.2791)	0.17487(0.1815)
N2_3	0.26063(0.2696)	-0.27146(-0.2723)	0.66805(0.6747)
N2_4	0.42532(0.4134)	0.60668(0.6072)	0.30222(0.3030)
a, b, c (Å)	7.07558458, 7.23618844, 7.28504275 (7.0802, 7.2306, 7.2554)		
α, β, γ (°)	88.792401, 84.887000, 75.963860(88.767, 84.733, 75.905)		

Note: The values in the parentheses represent the measured structural data [8b].

Table S4. Calculated structural data of Phase 2

	x/a	*y/b*	*z/c*
Ba1	-0.01433	0.2694	0.02763
Ba2	0.4841	0.7501	-0.02282
Ba3	0.4871	0.2539	0.5306
Sr	-0.001129	0.7814	0.4704
Si1_1	0.5388	0.4540	0.2074
Si1_2	0.02558	0.5634	0.7971
Si1_3	0.002500	0.05637	0.7022
Si1_4	0.5410	0.9574	0.3021
Si2_1	0.5278	0.2571	0.8029
Si2_2	0.04025	0.7650	0.2023
Si2_3	0.04272	0.2723	0.3078
Si2_4	0.5238	0.7540	0.6980
O1_1	0.4867	0.3770	0.09854
O1_2	-0.01813	0.6358	0.9068
O1_3	-0.01723	0.1100	0.5916
O1_4	0.4940	0.8827	0.4101
N1_1	0.8955	0.4815	0.2306
N1_2	0.3801	0.5380	0.7727
N1_3	0.3782	0.03633	0.7291
N1_4	0.8986	0.9832	0.2806
N2_1	0.3936	0.7404	0.2271
N2_2	0.8769	0.2798	0.7737
N2_3	0.8751	0.7770	0.7253
N2_4	0.3948	0.2421	0.2820
O2_1	0.4648	0.7079	0.5871
O2_2	-0.008065	0.3423	0.4174
O2_3	-0.01720	0.8116	0.09191
O2_4	0.4826	0.2139	0.9141
a, b, c (Å)	4.79587, 5.49709, 14.22931		
α, β, γ(°)	91.1187, 90.42157, 89.99789		

Note: the Rietveld refined structural data can be found in Table 2 and Table S1 (Supporting Information).

Table S5. Calculated structural data of Phase 3

	x/a	*y/b*	*z/c*
Ba	0 (0)	0.2440 (0.2497)	0.2500 (0.2500)
Si	0.8008 (0.7979)	0.3366 (0.3360)	0.6968 (0.709)
O	0.9085 (0.9057)	0.2593 (0.231)	0.7514 (0.740)
N	0.7195 (0.7244)	0.1328 (0.1224)	0.8421 (0.860)
a, b, c (Å)	14.31446, 5.30529, 4.83972 (14.3902, 5.34330, 4.83254)		

Note: The values in the parentheses represent the measured structural data [8c].

Table S6. Calculated structural data of Phase 1

Vector	Length (Å)	Optr cell	Neighbor atom coordinates		
Sr1_Sr2	3.88235(10)	1-100	-0.35127	0.2262	0.31813
Sr1_Sr2	4.24300(9)	1000	0.64873	0.2262	0.31813
Sr1_Sr3	3.64278(8)	1000	0.16512	0.11617	-0.43507
Sr1_Sr3	3.63676(8)	1001	0.16512	0.11617	0.56493
Sr1_Sr4	4.18320(10)	1-10-1	-0.35623	0.22399	-0.18158
Sr1_Sr4	3.89241(9)	100-1	0.64377	0.22399	-0.18158
Sr1_Sr5	4.00805(11)	10-10	0.24288	-0.43462	-0.0205
Sr1_Sr5	3.40542(9)	1000	0.24288	0.56538	-0.0205
Sr1_Sr6	3.79351(8)	1-100	-0.36087	0.11631	0.04262
Sr1_Sr6	3.31593(7)	1000	0.63913	0.11631	0.04262
Sr1_Sr7	1.90291(6)	1000	0.09219	0.23531	0.30265
Sr1_Sr8	4.64382(11)	100-1	0.64658	0.12241	-0.41586
Sr1_Si1	3.47158(15)	100-1	0.47397	-0.21199	-0.23071
Sr1_Si2	3.83557(10)	1000	0.3692	0.56683	0.09496
Sr1_Si4	3.64206(12)	1-100	-0.03207	-0.25716	0.27115
Sr1_Si5	3.31447(11)	100-1	0.0438	-0.20836	-0.16937
Sr1_Si6	3.75916(14)	1000	0.53886	-0.21446	0.32683
Sr1_N3	2.73293(7)	100-1	0.12662	-0.2405	0.05389
Sr1_O1	2.13240(6)	1000	0.32958	0.3359	0.07355
Sr1_O2	2.48668(8)	100-1	0.42882	-0.01166	-0.1819
Sr1_O3	2.82842(9)	1-100	-0.03984	-0.05876	0.33029
Sr1_O4	2.54097(9)	1000	-0.17218	0.3405	0.0799
Sr1_O5	2.86008(7)	100-1	-0.05612	-0.01898	-0.17919
Sr1_O6	2.89375(9)	1000	0.43937	-0.02492	0.33709

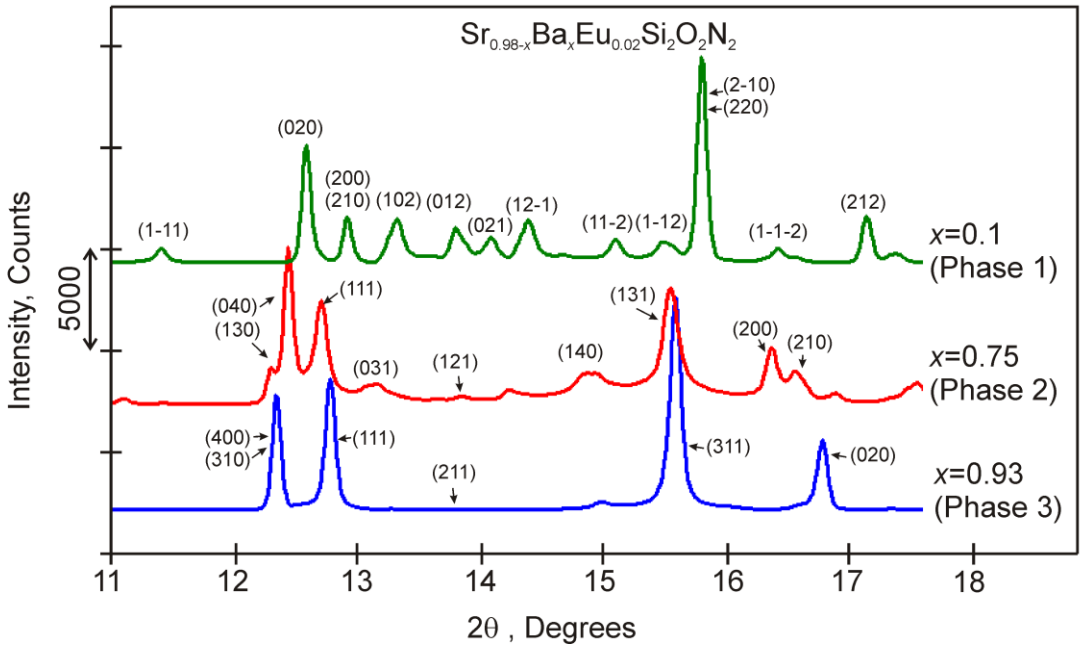


Figure S1. The representative high-resolution XRD patterns recorded over local angle range (11^{o}-18^{o}) for $(Sr_{0.98-x}Ba_xEu_{0.02})Si_2O_2N_2$ (x = 0.1, x = 0.75 and x = 0.93).

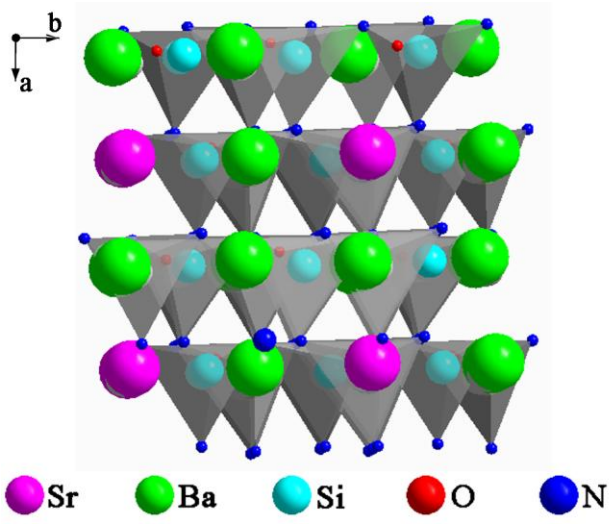
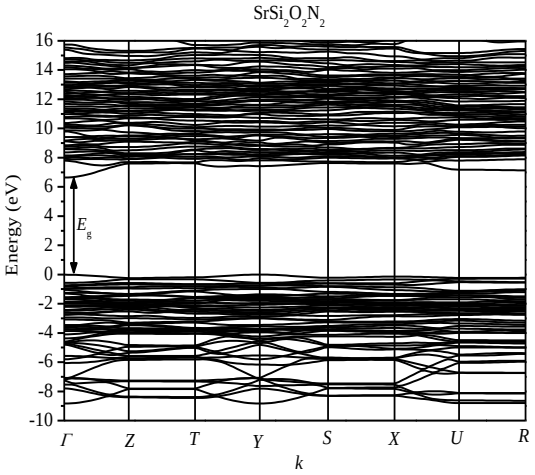
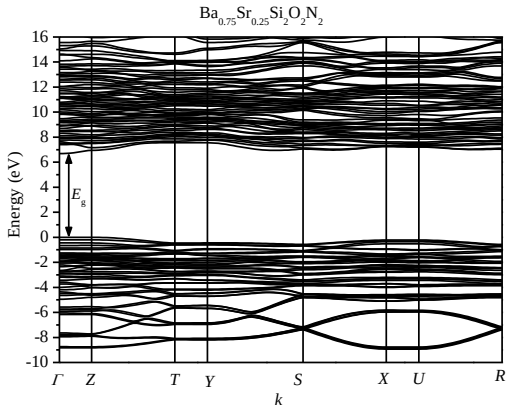


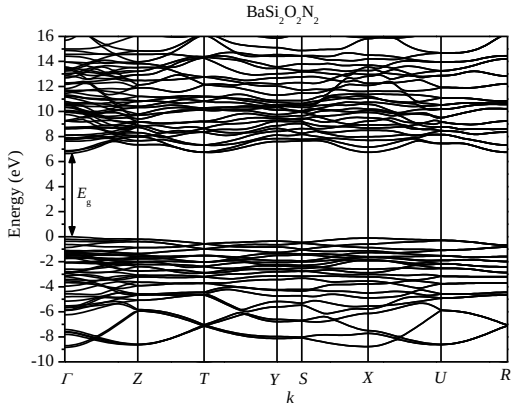
Figure S2. Structural schematic diagrams perpendicular to the stacking direction of $(Sr_{0.98-x}Ba_xEu_{0.02})Si_2O_2N_2$ samples (x = 0.68 to 0.77, Phase 2). Silicate layers of condensed $SiON_3^-$ tetrahedra (gray), Sr atoms (magenta), Ba atoms (green), Si atoms (cyan), O atoms (red), and N atoms (blue). (a and c axes are changed in Figure S2 compared with Scheme 1b)



a)



b)



c)

Figure S3. Calculated band structures for the three phases: (a) $SrSi_2O_2N_2$, (b) $Ba_{0.75}Sr_{0.25}Si_2O_2N_2$, and (c) $BaSi_2O_2N_2$. The letters *Γ*, *Z*, *T*, *Y*, *S*, *X*, *U*, and *R* represent the chosen *k* points: (0,0,0), (0,0,1/2), (0,1/2,1/2), (0,1/2,0), (1/2,1/2,0), (1/2,0,0), (1/2,0,1/2), and (1/2,1/2,1/2), respectively.

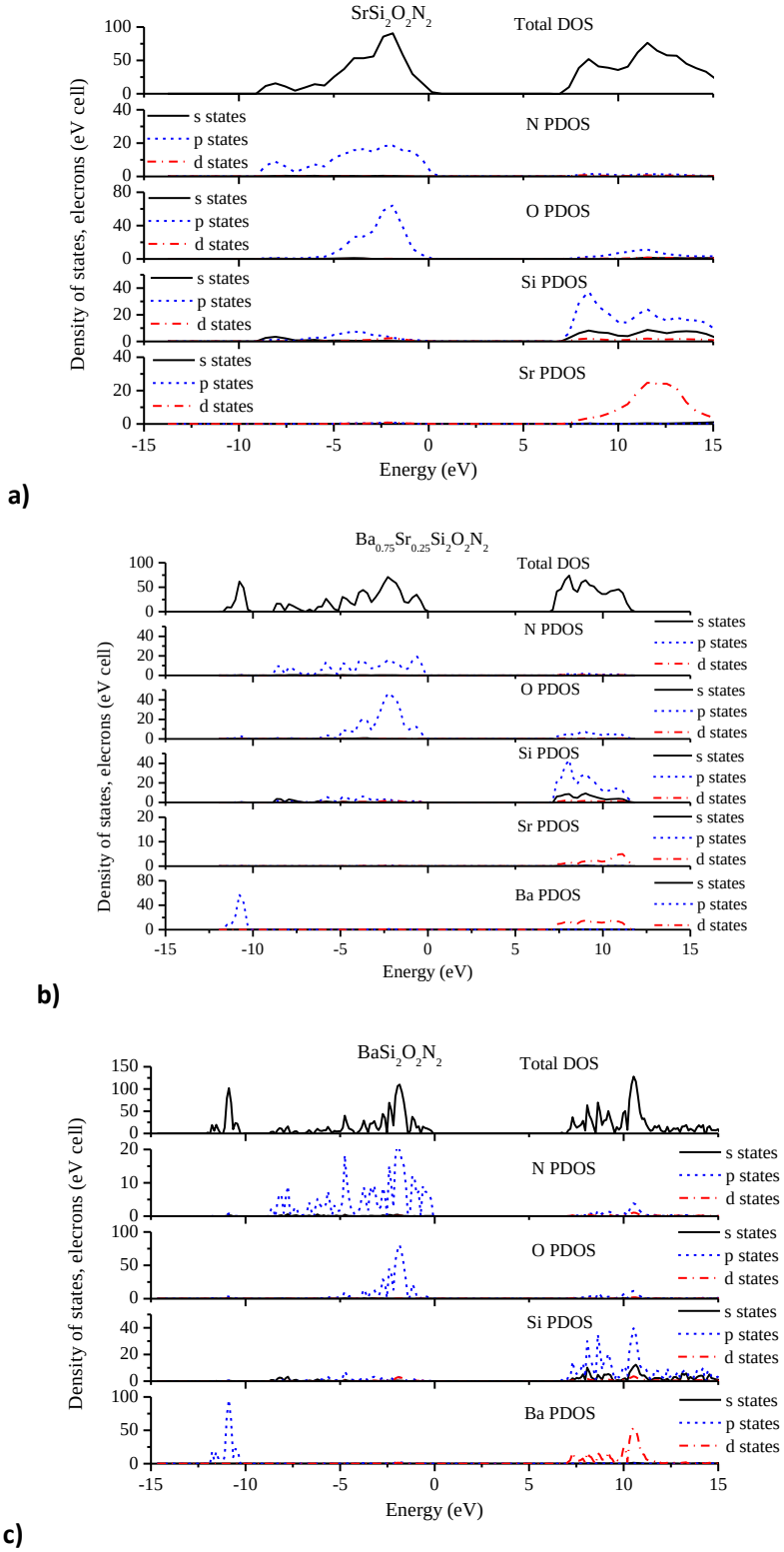


Figure S4. Calculated PDOS/TDOS diagrams for the three phases: (a) $SrSi_2O_2N_2$, (b) $Ba_{0.75}Sr_{0.25}Si_2O_2N_2$, and (c) $BaSi_2O_2N_2$.

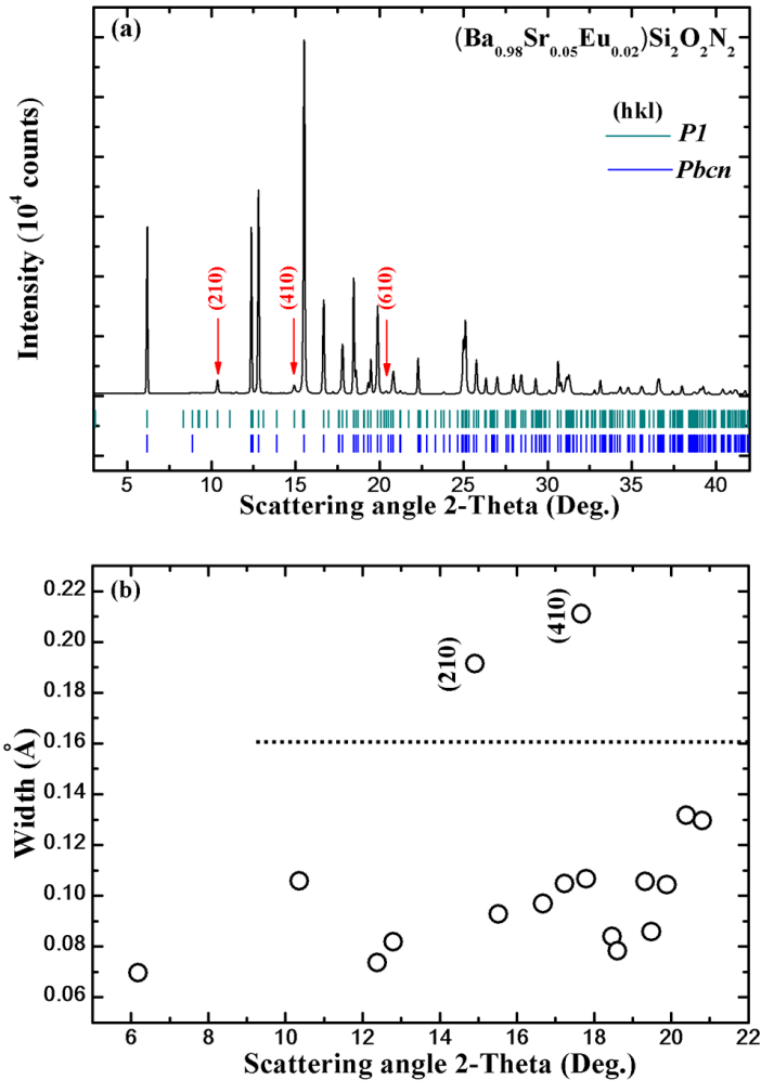


Figure S5. (a) The profile matching for XRD pattern of the representative $(Sr_{0.05}Ba_{0.93}Eu_{0.02})Si_2O_2N_2$ sample assuming the *P1* symmetry. (b) The peak widths of (2 1 0) and (4 1 0) are about twice of the other diffraction peaks.