Supplementary material for

Synthesis of $Ba_{1-x}Sr_xYSi_2O_5N$ and Discussion based on Structure Analysis and DFT Calculation

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Table S1. Contents in atomic% of cations in single crystals determined by EDX analysis.

		Ba	Sr	Y	Si
$x = 0$	Measured	21.0	0	28.1	51.0
	Ideal	25.0	0	25.0	50.0
$x = 0.1$	Measured	20.3	2.4	27.3	50.0
	Ideal	22.5	2.5	25.0	50.0
$x = 0.33$	Measured	12.3	7.7	28.3	51.6
	Ideal	16.7	8.3	25.0	50.0
$x = 0.50$	Measured	9.8	11.6	26.3	52.3
	Ideal	12.5	12.5	25.0	50.0
$x = 0.75$	Measured	5.4	16.8	27.9	50.0
	Ideal	6.3	18.8	25.0	50.0

Table S2. Bond length of *AE*–(O,N) and Y-(O,N).

	$x = 0$	$x = 0.1$	$x = 0.33$	$x = 0.5$	$x = 0.75$
Bond	Length / Å	Length / Å	Length / Å	Length / Å	Length / Å
			*AE*1		
–(O,N)1	2.659(5)	2.659(3)	2.641(3)	2.629(5)	2.592(7)
–(O,N)2	3.278(5)	3.286(3)	3.271(4)	3.260(5)	3.220(8)
–(O,N)4	2.795(5)	2.789(3)	2.765(4)	2.743(5)	2.708(8)
–(O,N)5	2.925(4)	2.918(3)	2.893(4)	2.881(4)	2.847(8)
–(O,N)6	2.891(6)	2.888(4)	2.892(4)	2.908(6)	2.909(9)
–(O,N)6	2.919(5)	2.919(3)	2.922(4)	2.919(5)	2.882(9)
–(O,N)7	2.783(4)	2.780(3)	2.762(3)	2.747(4)	2.697(6)
–(O,N)7	2.801(5)	2.795(3)	2.792(4)	2.788(5)	2.745(7)
–(O,N)9	3.257(6)	3.252(4)	3.255(5)	3.270(6)	3.280(10)
Ave.	2.92	2.92	2.91	2.91	2.88
			*AE*2		
–(O,N)1 × 2	2.683(4)	2.680(3)	2.649(4)	2.637(4)	2.602(6)
–(O,N)3 × 2	2.961(5)	2.961(3)	2.934(3)	2.904(5)	2.861(7)
–(O,N)5 × 2	2.655(5)	2.649(4)	2.614(4)	2.594(5)	2.568(7)
–(O,N)8 × 2	2.997(5)	3.002(4)	3.004(4)	3.010(5)	2.984(9)
–(O,N)9 × 2	2.901(6)	2.896(4)	2.891(5)	2.890(6)	2.877(9)
Ave.	2.84	2.84	2.82	2.81	2.78
			Y1		
–(O,N)1	2.263(5)	2.262(3)	2.263(3)	2.271(5)	2.264(7)
–(O,N)2	2.323(4)	2.320(3)	2.320(4)	2.317(4)	2.318(8)
–(O,N)2	2.348(5)	2.346(3)	2.344(4)	2.343(5)	2.320(8)
–(O,N)3	2.254(4)	2.255(3)	2.252(3)	2.263(4)	2.258(6)
–(O,N)4	2.266(5)	2.267(3)	2.269(4)	2.272(5)	2.264(7)
–(O,N)7	2.272(5)	2.272(3)	2.268(4)	2.276(5)	2.283(7)
Ave.	2.29	2.29	2.29	2.29	2.28
			Y2		
–(O,N)3 × 2	2.469(4)	2.462(3)	2.455(3)	2.459(4)	2.447(6)
–(O,N)4 × 2	2.536(4)	2.544(3)	2.530(4)	2.537(4)	2.526(7)
–(O,N)5 × 2	2.428(5)	2.425(4)	2.443(4)	2.456(5)	2.455(7)
–(O,N)9 × 2	2.301(6)	2.302(4)	2.305(5)	2.333(6)	2.311(10)
Ave.	2.43	2.43	2.43	2.45	2.43

Table S3. Refinement parameters obtained using the model with g(Sr, AE1) = 0.625.

g(Sr, AE1)	0.625[1]	0.6420(3)[2]
GoF	1.251	1.257
R, wR [$F^2 > 2\sigma(F^2)$]	4.66%, 10.63%	4.63%, 10.58%
R, wR (F^2)	5.21%, 10.87%	5.18%, 10.82%
Min./ max. residual electron density / eÅ^{-3}	1.119, −1.223	1.128, −1.237

[1] The value was fixed. [2] The value was refined.

Table S4. Results of geometry optimization for x = 0 and 1. The lattice parameters are a, b = 6.65670 Å (6.66510 Å), c = 18.81460 Å (18.49490 Å), α, β = 96.7436º (96.9847º), and γ = 101.0314º (101.3262º) for X = 0 (X = 1).

x = 0 (Space group: Cc)				x = 1 (Space group: Cc)			
Atom	x	y	z	Atom	x	y	z
Ba	-0.20623	0.57238	0.58192	Sr	-0.21121	0.56657	0.58574
Ba	0.21952	1.41841	0.42357	Sr	0.2408	1.40404	0.42296
Ba	0.08952	0.91384	0.74881	Sr	0.09942	0.90223	0.74805
Y	0.01288	1.60853	0.91686	Y	0.02084	1.62268	0.91762
Y	-0.01921	0.39116	0.08339	Y	-0.03037	0.37869	0.08227
Y	-0.35287	1.34954	0.74956	Y	-0.35866	1.35164	0.74982
Si	0.29233	1.47638	0.61043	Si	0.28771	1.46782	0.60785
Si	-0.29216	0.53018	0.3919	Si	-0.28514	0.53946	0.395
Si	-0.06644	1.12816	0.59614	Si	-0.07441	1.12023	0.59797
Si	0.06762	0.87155	0.40302	Si	0.07583	0.87984	0.40071
Si	0.11625	1.41037	0.73533	Si	0.11095	1.40617	0.73606
Si	-0.11481	0.59579	0.26261	Si	-0.11091	0.6002	0.26119
O	0.05838	0.93866	0.59911	O	0.04701	0.92873	0.60456
O	-0.05909	1.05937	0.39794	O	-0.04743	1.06974	0.3919
O	-0.29124	1.04196	0.54193	O	-0.29723	1.03098	0.54308
O	0.29049	0.95929	0.45715	O	0.29651	0.97867	0.45553
O	-0.00381	1.51323	0.79845	O	0.00118	1.52505	0.79964
O	0.00262	0.48193	0.20335	O	-0.00287	0.46906	0.2026
O	0.46341	1.32922	0.62626	O	0.46422	1.32648	0.6229
O	-0.46357	0.66747	0.37303	O	-0.46511	0.66818	0.37736
O	0.30204	1.31073	0.7765	O	0.2843	1.29317	0.77897
O	-0.3026	0.69255	0.22647	O	-0.28629	0.71024	0.22244
O	0.08323	1.30987	0.55542	O	0.07657	1.29631	0.55453
O	-0.08254	0.68777	0.44319	O	-0.0755	0.70407	0.44398
O	-0.614	0.63772	0.55615	O	-0.62244	0.62577	0.55104
O	0.62079	1.35651	0.44032	O	0.63455	1.36682	0.44571
O	-0.20804	0.42965	0.31996	O	-0.21415	0.43768	0.31907
N	0.20165	1.58706	0.68042	N	0.20593	1.58129	0.68085
N	-0.09486	1.23623	0.68011	N	-0.1052	1.23999	0.68066
N	0.0925	0.75272	0.3207	N	0.10097	0.74831	0.31992

Table S5. Absorption rate, internal quantum efficiency (IQE), and external quantum efficiency (EQE) of 2 mol% Eu- or Ce-doped $Ba_{1-x}Sr_xYSi_2O_5$ (x = 0, 0.1, 0.33, 0.5, and 0.75).

Sample		Abs. %	IQE %	EQE %
2 mol% Eu λ_{ex} = 340 nm	X = 0	76.0	25.9	19.7
	X = 0.1	73.1	27.4	20.0
	X = 0.33	76.9	22.6	17.4
	X = 0.5	81.2	20.2	16.4
	X = 0.75	73.4	15.6	11.4
2 mol% Ce λ_{ex} = 345 nm	X = 0	66.2	43.5	28.8
	X = 0.1	77.3	40.2	31.1
	X = 0.33	70.0	39.3	27.6
	X = 0.5	74.1	36.3	26.9
	X = 0.75	72.6	30.5	22.2

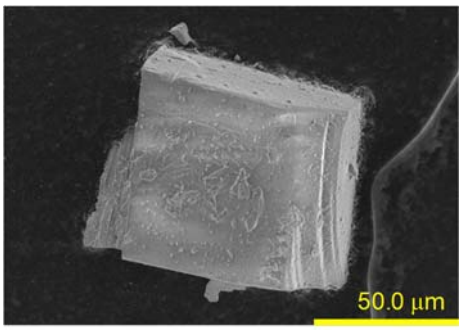


Figure S1. A SEM image of a $BaYSi_2O_5N$ single crystal.

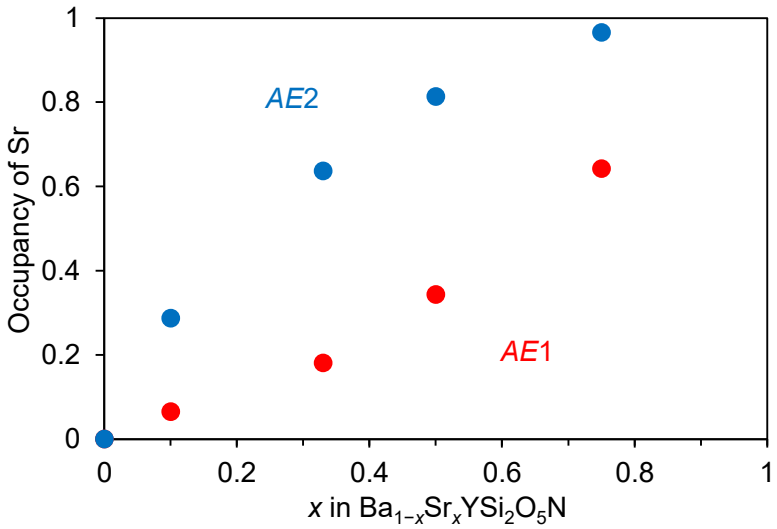


Figure S2. Occupancy of Sr at two *AE* sites.

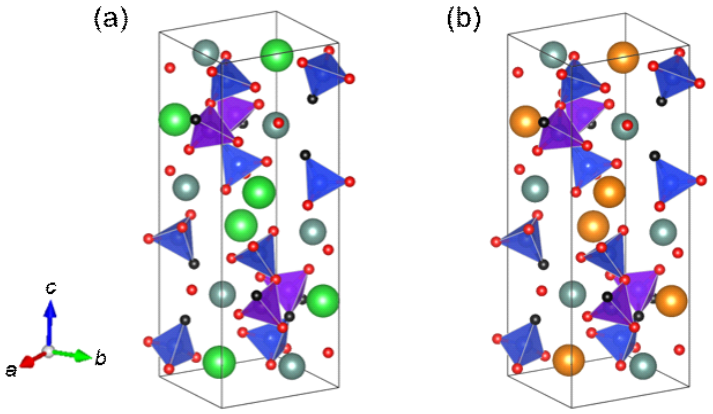


Figure S3. Models used for phonon calculation of (a) $x = 0$ and (b) $x = 0.75$ with Ba (green), Sr (orange), Y (gray), Si1, Si2 (blue), Si3 (purple), O (red), and N(black). Si3B site was deleted and Si3A was fully occupied by Si, and anion occupancies were determined in terms of bond length, resulting in formation of a $Si_3O_7N_2$ ring. At the

same time, site symmetry can be changed to *Cc* from *C*2/*c*. To save machine time, *Cc* was applied.

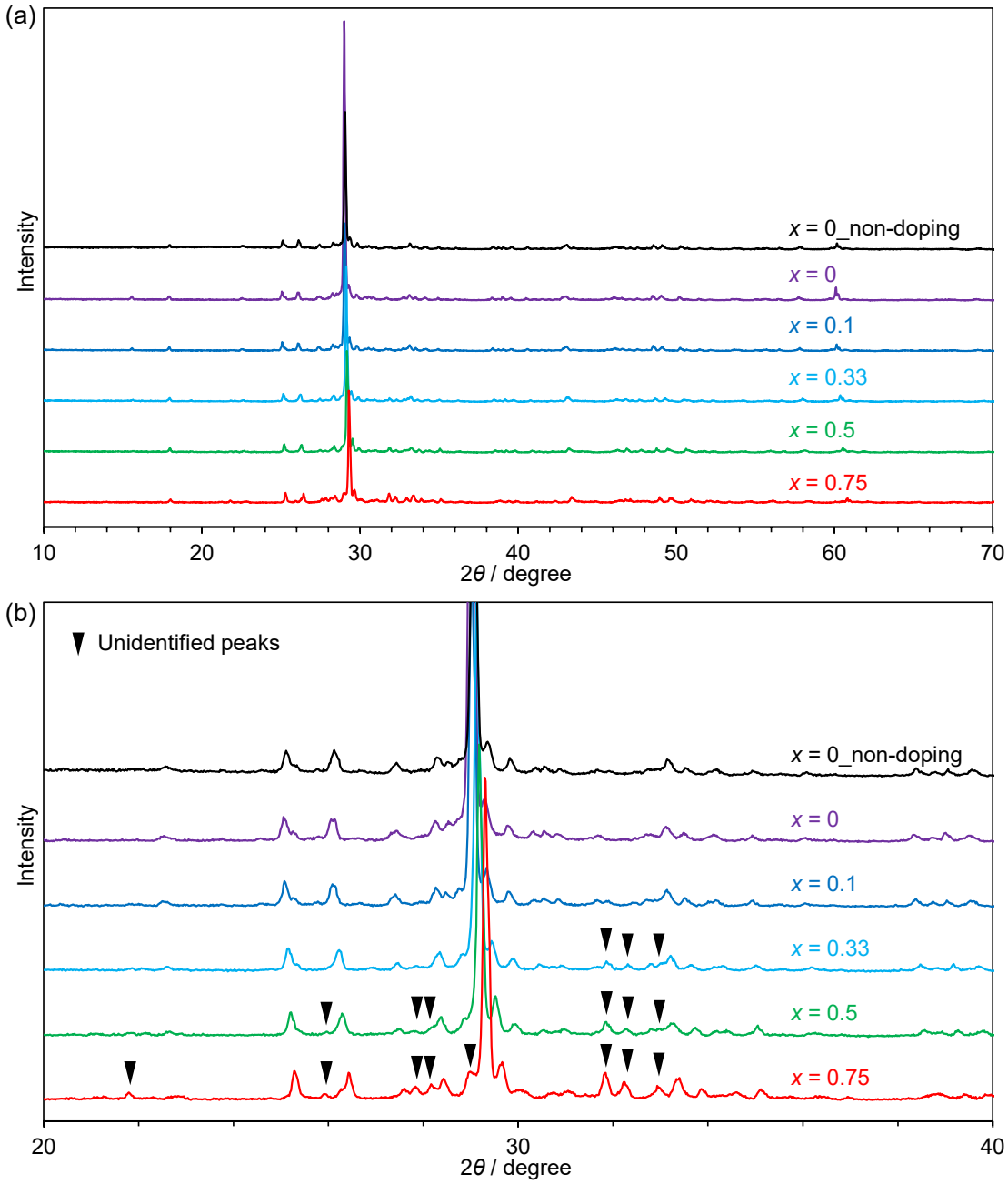


Figure S4. XRD patterns of 2 mol% Eu-doped $Ba_{1-x}Sr_xYSi_2O_5N$ (x = 0, 0.1, 0.33, 0.5, and 0.75) samples. (b) was a magnified pattern in the range of 2θ = 20º–30º.

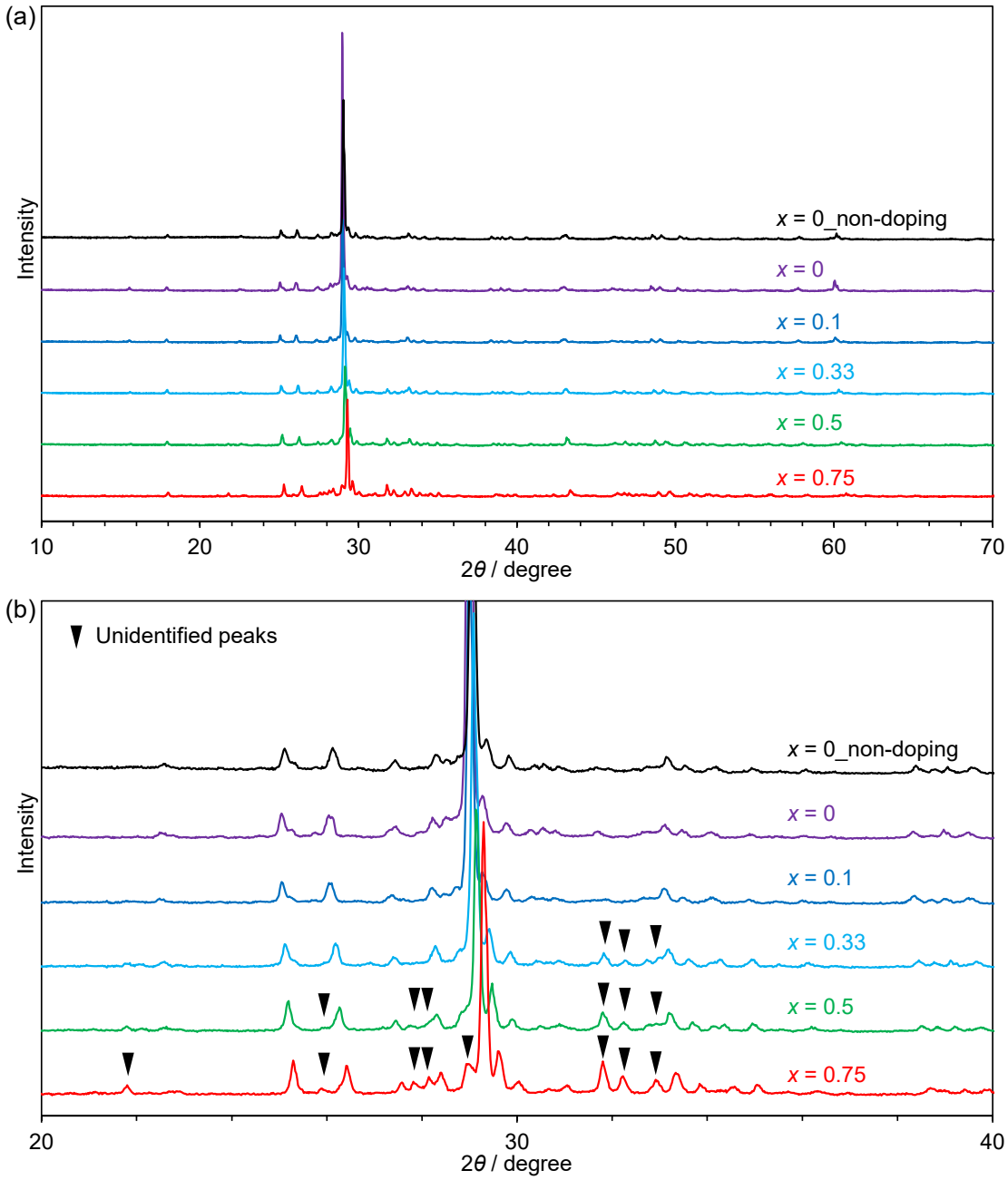


Figure S5. XRD patterns of 2 mol% Ce-doped $Ba_{1-x}Sr_xYSi_2O_5N$ (x = 0, 0.1, 0.33, 0.5, and 0.75) samples. (b) was a magnified pattern in the range of 2θ = 20º–30º.

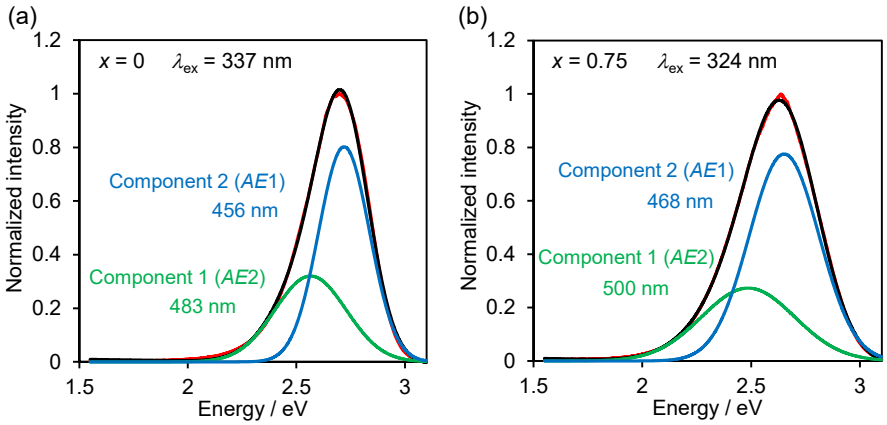
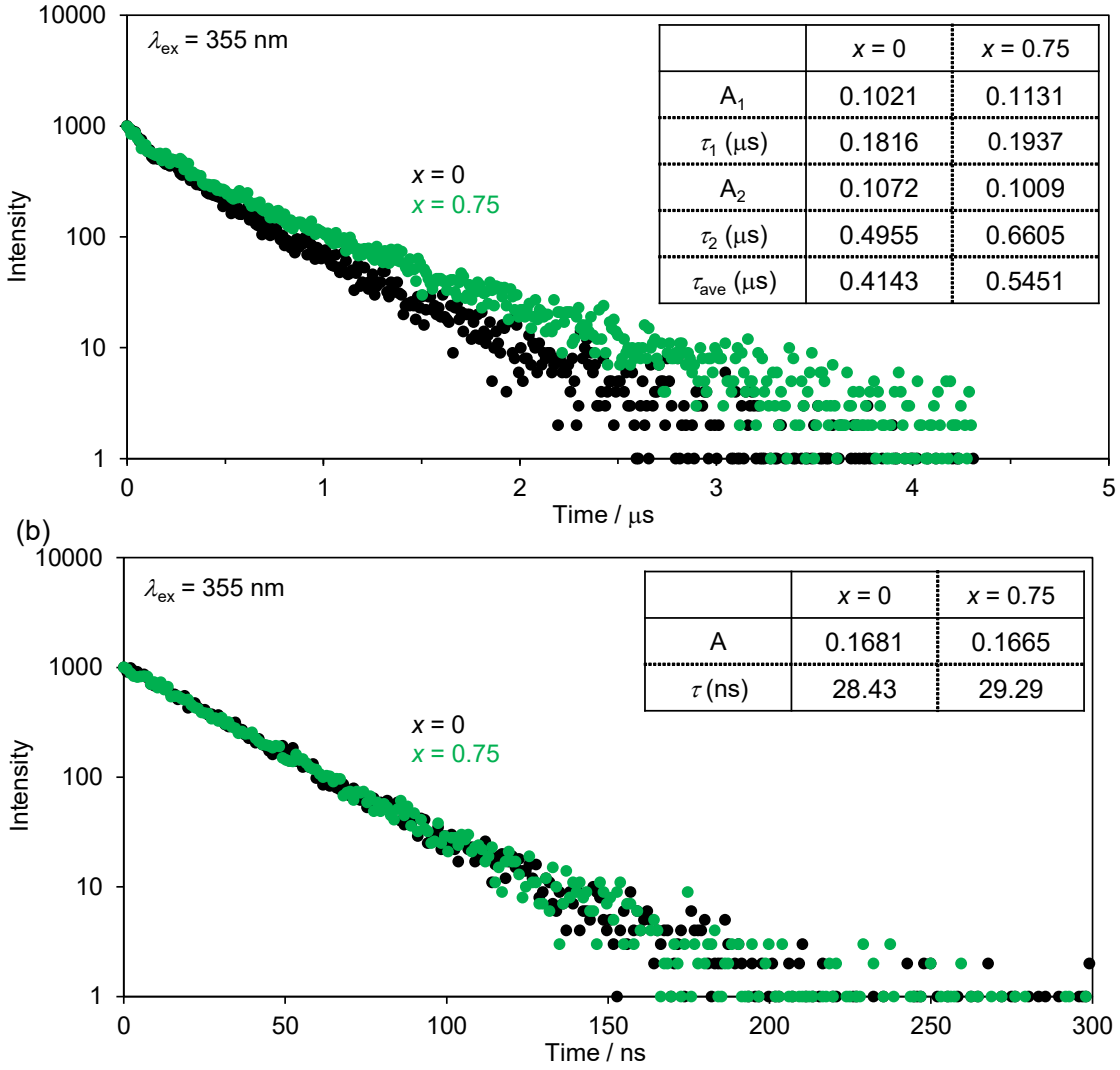


Figure S6. Decomposition of emission curves of Eu-doped samples at (a) x = 0 and (b) 0.75. Red, black, blue, and green curves are observed, fitting, component 1 and component 2 curves, respectively.



	x = 0	x = 0.75
A_1	0.1021	0.1131
τ_1 (μs)	0.1816	0.1937
A_2	0.1072	0.1009
τ_2 (μs)	0.4955	0.6605
τ_{ave} (μs)	0.4143	0.5451

	x = 0	x = 0.75
A	0.1681	0.1665
τ (ns)	28.43	29.29

Figure S7. Luminescence decay curves of x = 0 and 0.75 samples with 2 mol% Eu activation.

The decay curves of Eu-doped samples can be fitted by the following double exponential equation:

$$I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad \text{(S1)}$$

where I is the luminescence intensity, A_1 and A_2 are constants, t is the time, and τ_1 and τ_2 are the decay times for the exponential components. The average decay times (τ_{ave}) can be calculated by the following equation:

$$\tau_{ave} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2) \quad \text{(S2)}$$

τ_{ave} are reasonable in comparison to other phosphors with Eu activation [1,2].

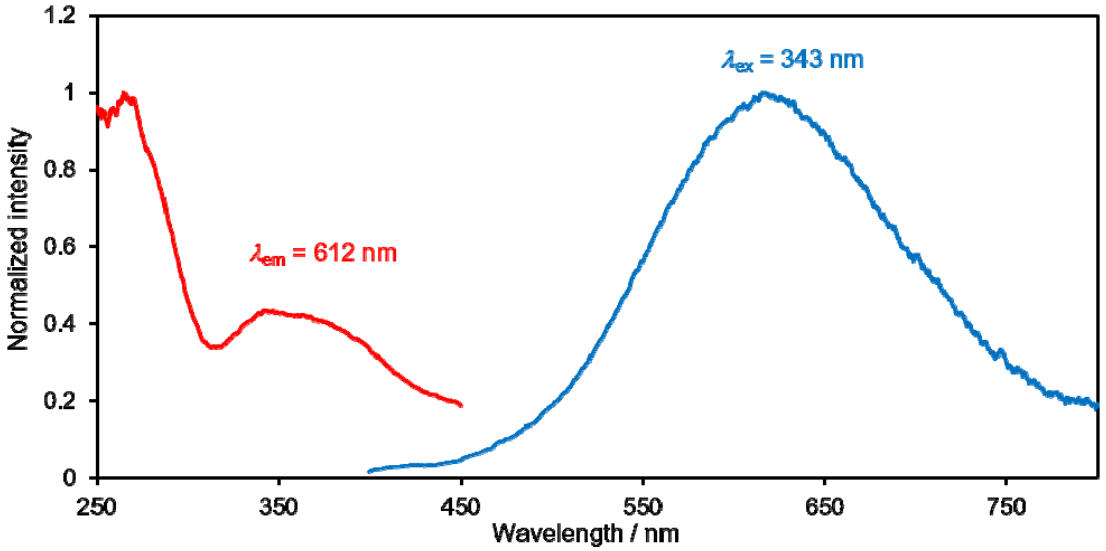


Figure S8. PL and PLE spectra of the 2 mol% Eu-doped sample synthesized at $x = 1$.

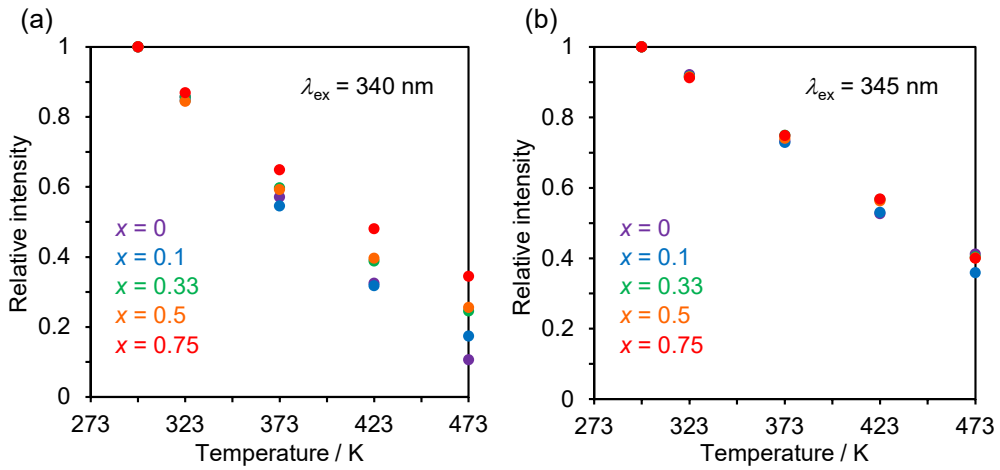


Figure S9. Temperature dependence of PL intensity of 2 mol% (a) Eu- or (b) Ce-doped $Ba_{1-x}Sr_xYSi_2O_5N$ ($x = 0$, 0.1, 0.33, 0.5, and 0.75) powders.

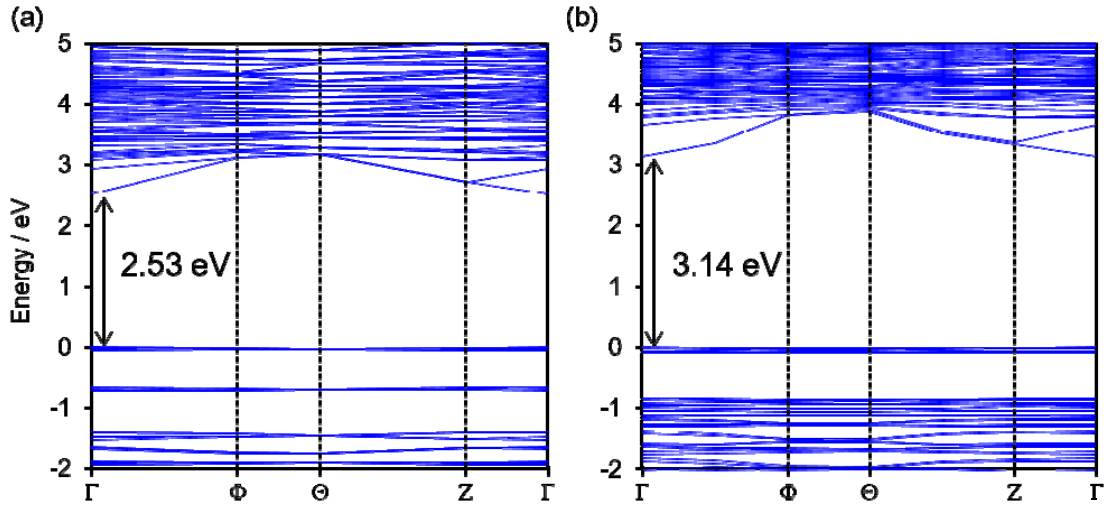


Figure S10. Band structures of (a) $BaYSi_2O_5N$ (x = 0) and (b) $Ba_{0.25}Y_{0.75}YSi_2O_5N$ (x = 0.75). Conduction and valence bands were composed of Ba 5*d*, Sr 4*d*, and Y 4*d*, and O and N 2*p* orbitals, respectively.

References

(1) V. Bachmann, C. Ronda, O. Oeckler, W. Schnick, A. Meijerink, Color Point Tuning for (Sr,Ca,Ba)$Si_2O_2N_2$:Eu^{2+} for White Light LEDs, *Chem. Mater.* 21 (2009) 316−325.

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