

Supporting Information

Enhanced Photoluminescence Emission and Thermal Stability from Introduced Cation Disorder in Phosphors

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EXPERIMENTAL METHODS

Synthesis.

A series of nitridosilicates $\text{Sr}_{1.98-x}(\text{Ca}_{0.55}\text{Ba}_{0.45})_x\text{Si}_5\text{N}_8:\text{Eu}_{0.02}$ ($x = 0, 0.5, 1.0, 1.5$, and 1.98) was synthesized from a stoichiometric mixture of Sr_3N_2 (Materion, 99.5%), Ca_3N_2 (Cerac, 99.0%), Ba_3N_2 (Cerac, 99.5%), EuN (Cerac, 99.9%), and $\alpha\text{-Si}_3\text{N}_4$ [Ube Industries, grade SN-E10, $\alpha/(\alpha+\beta) > 95\%$ by weight] by a solid-state reaction. The elemental precursors were weighed and ground in an argon-filled glove box ($\text{H}_2\text{O} < 1$ ppm, $\text{O}_2 < 1$ ppm). The mixtures were transferred into boron nitride crucibles and placed in a gas pressure sintering furnace (FVPHP-R-5, FRET-25, Fujidempa Kogyo Co., Ltd.). The temperature was increased from room temperature to 1600°C with a heating rate of $30^\circ\text{C}/\text{min}$ under 0.51 MPa N_2 atmosphere and was maintained for 2 h. Reddish samples were formed, and they were ground in an agate mortar for measurements. The $x = 1.98$ sample was found to be a multiphase mixture and was not explored further, but the other four samples were studied as below.

Characterizations.

Synchrotron XRD patterns with wavelength of $0.774907\text{ \AA}$ were recorded at the BL01C2 beamline of the National Synchrotron Radiation Research Center, Taiwan. Neutron diffraction data were collected from 2 g samples of $\text{Sr}_{1.98-x}(\text{Ca}_{0.55}\text{Ba}_{0.45})_x\text{Si}_5\text{N}_8:\text{Eu}_{0.02}$ samples with $x = 0, 0.5, 1.0$, and 1.5 , at $25, 100, 200, 300$, and 400°C on the POWGEN instrument at the SNS facility, USA. Rietveld refinements were made using the general structure analysis system GSAS.¹ Electron microscopy investigations were performed on a JEOL JEM-2011 electron microscope, operating at a voltage of 200 kV . SAED patterns and HRTEM images were recorded with a Gatan 794 CCD camera. The morphology of the as-prepared samples was investigated using a Nova NanoSEM 450 (FEI, Oregon, USA) equipped with high-resolution field-emission scanning electron microscope at 10 kV . The chemical compositions of selected samples were analyzed by EDX spectroscopy using a Bruker SDD-EDS detector. Excitation and emission spectra were obtained on a FluoroMax-3 spectrophotometer equipped with a 150 W Xe lamp and Hamamatsu R928 photomultiplier tube. The quantum efficiency (QE) of $\text{Sr}_{1.98-x}(\text{Ca}_{0.55}\text{Ba}_{0.45})_x\text{Si}_5\text{N}_8:\text{Eu}_{0.02}$ samples was determined using a HORIBA Jobin-Yvon spectrofluorimeters with an optical integrating sphere (diameter of 100 mm) showed a reflectance $> 99\%$ over $400\text{--}1500\text{ nm}$ range ($> 95\%$ within $250\text{--}2500\text{ nm}$).² The accessories were made from Teflon (rod and sample holders) or Spectralon (baffle). Temperature-dependent PL emission spectra were accessed using a THMS-600 heating attachment. PL decay curves were recorded by an Edinburgh FLS920 spectrometer at room temperature at an excitation wavelength of 460 nm , using a gated hydrogen arc lamp and a scatter solution to profile the instrument response function. In the TL experiments, the sample was radiated by a

254 nm mercury lamp for 5 min and the TL spectra were recorded promptly by a RISØDA-15B/C TL/PL spectrometer from 25 to 300 °C with a heating rate at 5 °C/s. Raman spectra were measured by a Nicolet Almega XR Raman spectrometer with Olympus-BX51 Microscope.

Table S1. Refined lattice parameters in Å from room temperature refinements of $\text{Sr}_{1.98-x}(\text{Ca}_{0.55}\text{Ba}_{0.45})_x\text{Si}_5\text{N}_8:\text{Eu}_{0.02}$ ($x = 0, 0.5, 1.0, 1.5$) using synchrotron data.

x	0	0.5	1.0	1.5
a (Å)	5.6952(2)	5.6963(1)	5.6950(1)	5.6999(3)
b (Å)	6.8023(2)	6.8056(1)	6.8012(2)	6.7989(4)
c (Å)	9.3081(3)	9.3053(2)	9.3015(2)	9.3062(5)
V (Å ³)	360.60(2)	360.74(2)	360.28(2)	360.65(5)

Table S2. Refined atomic parameters from room temperature refinements of $\text{Sr}_{1.98-x}(\text{Ca}_{0.55}\text{Ba}_{0.45})_x\text{Si}_5\text{N}_8:\text{Eu}_{0.02}$ ($x = 0, 0.5, 1.0, 1.5$) using powder neutron and synchrotron data.

x = 0

	x	y	z	U_{iso} (Å²)
M1	0	0.8631(9)	-0.0061(8)	0.0078(7)
M2	0	0.8816(9)	0.3637(7)	0.0078(7)
Si1	0.2476(11)	0.6653(6)	0.6749(7)	0.0005(4)
Si2	0	0.0548(10)	0.6762(11)	0.0005(4)
Si3	0	0.4189(14)	0.4573(9)	0.0005(4)
Si4	0	0.411(2)	0.9001(9)	0.0005(4)
N1	0	0.1851(6)	0.5211(6)	0.0051(2)
N2	0.2476(6)	0.9131(3)	0.6676(4)	0.0051(2)
N3	0.2494(8)	0.4455(3)	0.0075(3)	0.0051(2)
N4	0	0.5858(7)	0.7701(5)	0.0051(2)
N5	0	0.1768(8)	0.8333(6)	0.0051(2)
N6	0	0.4210(7)	0.2662(6)	0.0051(2)

$\chi^2 = 7.51$ and $R_{\text{wp}} = 6.21\%$

x = 0.5

	x	y	z	U _{iso} (Å ²)
M1	0	0.8673(9)	-0.0034(8)	0.0090(7)
M2	0	0.8807(9)	0.3659(8)	0.0090(7)
Si1	0.2495(11)	0.6646(6)	0.6791(6)	-0.0003(3)
Si2	0	0.0538(10)	0.6754(10)	-0.0003(3)
Si3	0	0.4218(13)	0.4592(8)	-0.0003(3)
Si4	0	0.4097(14)	0.9030(8)	-0.0003(3)
N1	0	0.1897(5)	0.5219(6)	0.0049(2)
N2	0.2477(6)	0.9121(3)	0.6667(4)	0.0049(2)
N3	0.2497(8)	0.4449(3)	0.0078(3)	0.0049(2)
N4	0	0.5874(6)	0.7716(5)	0.0049(2)
N5	0	0.1766(7)	0.8345(5)	0.0049(2)
N6	0	0.4224(7)	0.2685(5)	0.0049(2)

$\chi^2 = 6.16$ and $R_{wp} = 5.57\%$

x = 1.0

	x	y	z	U _{iso} (Å ²)
M1	0	0.8745(13)	-0.0012(11)	0.0104(10)
M2	0	0.8799(14)	0.3671(11)	0.0104(10)
Si1	0.2531(14)	0.6651(8)	0.6814(7)	-0.0008(4)
Si2	0	0.0545(12)	0.6753(12)	-0.0008(4)
Si3	0	0.4227(16)	0.4612(10)	-0.0008(4)
Si4	0	0.411(2)	0.9048(10)	-0.0008(4)
N1	0	0.1913(7)	0.5240(7)	0.0053(3)
N2	0.2479(7)	0.9114(4)	0.6662(5)	0.0053(3)
N3	0.2490(10)	0.4453(4)	0.0088(4)	0.0053(3)
N4	0	0.5877(8)	0.7730(7)	0.0053(3)
N5	0	0.1750(10)	0.8372(7)	0.0053(3)
N6	0	0.4242(8)	0.2700(7)	0.0053(3)

$\chi^2 = 9.64$ and $R_{wp} = 6.94\%$

x = 1.5

	x	y	z	U _{iso} (Å ²)
M1	0	0.882(2)	-0.0014(14)	0.011(2)
M2	0	0.882(2)	0.370(2)	0.011(2)
Si1	0.253(2)	0.6639(11)	0.6828(10)	0.0001(6)
Si2	0	0.060(2)	0.676(2)	0.0001(6)
Si3	0	0.426(2)	0.4605(14)	0.0001(6)
Si4	0	0.412(2)	0.9090(14)	0.0001(6)
N1	0	0.1912(10)	0.5255(10)	0.0064(4)
N2	0.2470(10)	0.9102(6)	0.6633(6)	0.0064(4)
N3	0.2484(14)	0.4469(6)	0.0102(6)	0.0064(4)
N4	0	0.5853(12)	0.7750(10)	0.0064(4)
N5	0	0.1771(14)	0.8364(10)	0.0064(4)
N6	0	0.4240(13)	0.2714(10)	0.0064(4)

$\chi^2 = 14.20$ and $R_{wp} = 8.18\%$

Table S3. Refined lattice parameters and cation site occupancies from room temperature refinements of $\text{Sr}_{1.98-x}(\text{Ca}_{0.55}\text{Ba}_{0.45})_x\text{Si}_5\text{N}_8:\text{Eu}_{0.02}$ ($x = 0, 0.5, 1.0, 1.5$) using powder neutron and synchrotron data. Derived global and site mean cation radii and size variances are also shown.

x	0	0.5	1.0	1.5
a (Å)	5.6994(1)	5.7003(1)	5.7019(1)	5.7011(2)
b (Å)	6.8087(2)	6.8100(1)	6.8069(2)	6.7965(3)
c (Å)	9.3122(2)	9.3098(2)	9.3134(3)	9.3102(3)
V (Å ³)	361.37(2)	361.40(2)	361.47(2)	360.75(3)
Eu1	0.01	0.01	0.01	0.01
Ca1	0.00	0.15(5)	0.47(5)	0.46(2)
Sr1	0.99	0.68(5)	0.21(5)	0.05(2)
Ba1	0.00	0.16(5)	0.31(5)	0.48
Eu2	0.01	0.01	0.01	0.01
Ca2	0.00	0.13(5)	0.08(5)	0.36(2)
Sr2	0.99	0.80(5)	0.77(5)	0.43(2)
Ba2	0.00	0.06(5)	0.14(5)	0.20
<r _{Sr} > (Å)	1.31	1.31	1.31	1.31
<r _{Sr1} > (Å)	1.31	1.32	1.30	1.33
<r _{Sr2} > (Å)	1.31	1.30	1.32	1.29
σ_{Sr}^2 (Å ²)	0.000	0.005	0.010	0.016
σ_{Sr1}^2 (Å ²)	0.000	0.007	0.016	0.020
σ_{Sr2}^2 (Å ²)	0.000	0.004	0.005	0.011

Table S4. Refined lattice parameters in Å from variable temperature refinements of $\text{Sr}_{1.98-x}(\text{Ca}_{0.55}\text{Ba}_{0.45})_x\text{Si}_5\text{N}_8:\text{Eu}_{0.02}$ ($x = 0, 0.5, 1.0, 1.5$) using powder neutron diffraction profiles.

x = 0				x = 0.5		
T (°C)	a	b	c	a	b	c
25	5.7074(1)	6.8211(2)	9.3197(2)	5.7087(1)	6.8189(2)	9.3200(2)
100	5.7102(1)	6.8239(2)	9.3231(2)	5.7111(1)	6.8213(2)	9.3232(2)
200	5.7137(1)	6.8270(2)	9.3274(2)	5.7144(2)	6.8245(2)	9.3277(2)
300	5.7167(1)	6.8308(2)	9.3318(3)	5.7177(1)	6.8280(2)	9.3324(2)
400	5.7196(1)	6.8350(2)	9.3361(3)	5.7206(1)	6.8321(2)	9.3373(2)

x = 1.0				x = 1.5		
T (°C)	a	b	c	a	b	c
25	5.7073(5)	6.8107(2)	9.3229(3)	5.7020(2)	6.7944(3)	9.3136(4)
100	5.7094(2)	6.8129(2)	9.3258(3)	5.7040(2)	6.7973(3)	9.3163(4)
200	5.7128(2)	6.8163(2)	9.3302(3)	5.7072(2)	6.8014(3)	9.3209(4)
300	5.7160(2)	6.8198(2)	9.3349(3)	5.7106(2)	6.8065(3)	9.3258(4)
400	5.7193(2)	6.8248(2)	9.3399(3)	5.7136(2)	6.8126(3)	9.3308(4)

Table S5. Photoluminescent properties of two crystallographic sites for $\text{Sr}_{1.98-x}(\text{Ca}_{0.55}\text{Ba}_{0.45})_x\text{Si}_5\text{N}_8:\text{Eu}_{0.02}$ ($x = 0, 0.5, 1.0, 1.5$) samples.

x	Sr1			Sr2		
	Max. position (cm^{-1})	Relative Intensity (%)	FWHM (cm^{-1})	Max. position (cm^{-1})	Relative Intensity (%)	FWHM (cm^{-1})
0	16,414	100	1,817	15,523	100	2,421
0.5	16,342	92	1,933	15,379	115	2,590
1.0	16,277	75	2,046	15,300	144	2,688
1.5	16,148	56	2,176	15,214	173	2,733

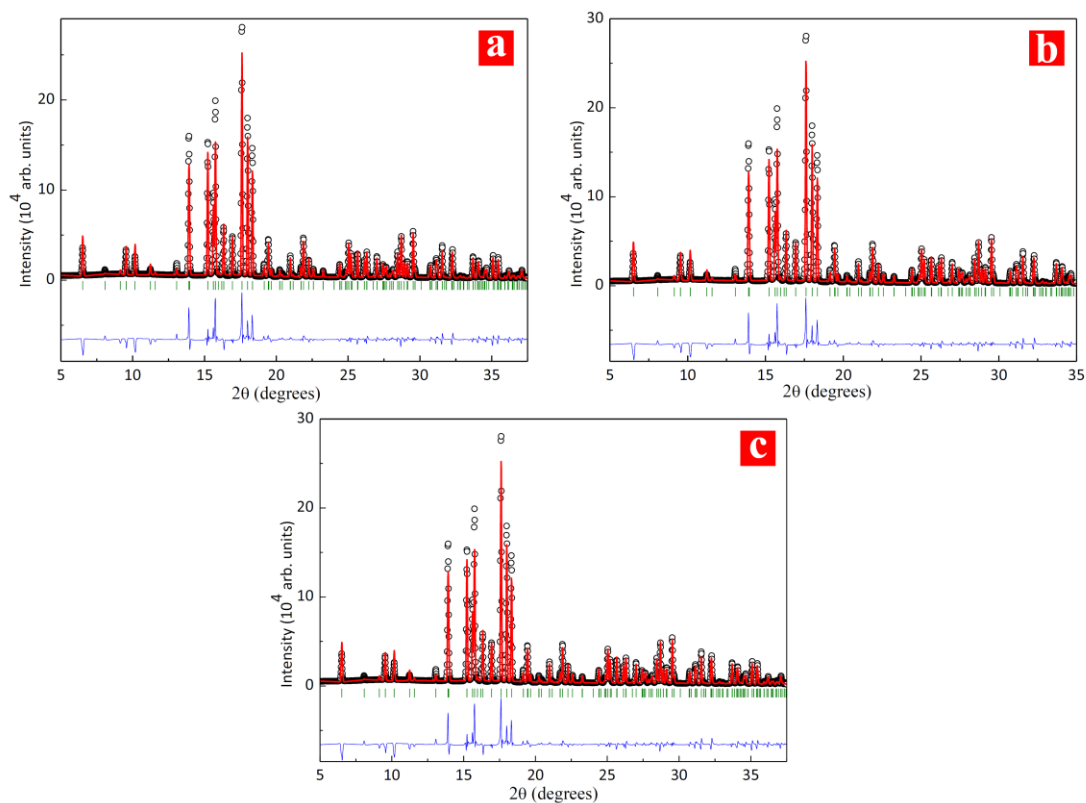


Figure S1. Rietveld refinement of the $\text{Sr}_{1.98-x}(\text{Ca}_{0.55}\text{Ba}_{0.45})_x\text{Si}_5\text{N}_8:\text{Eu}_{0.02}$ at room temperature powder diffraction profiles; synchrotron X-ray diffraction pattern from the BL01C2 beamline with wavelength of $0.774907\text{\AA}$ at the NSRRC. (a) $x = 0$, (b) $x = 1.0$, and (c) $x = 1.5$.

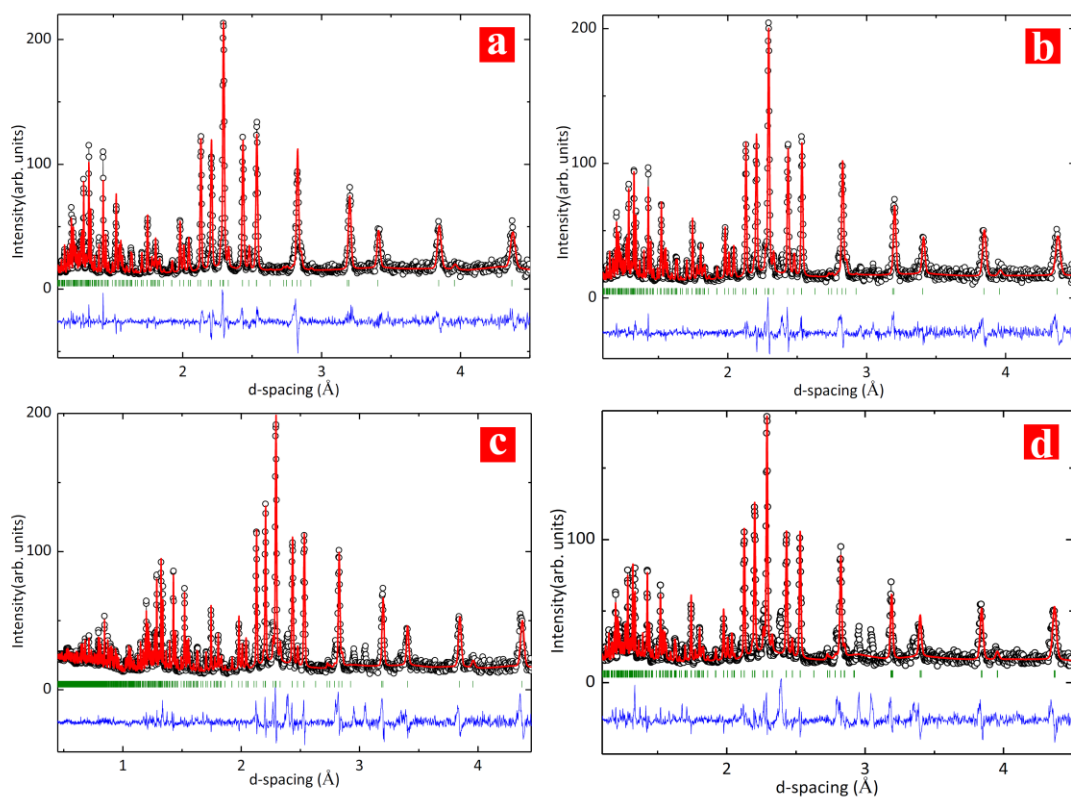


Figure S2. Neutron room temperature refinements from the POWGEN beamline at SNS using the $\lambda = 1.066$ Å bank for $\text{Sr}_{1.98-x}(\text{Ca}_{0.55}\text{Ba}_{0.45})_x\text{Si}_5\text{N}_8:\text{Eu}_{0.02}$ (a) $x = 0$, (b) $x = 0.5$, (c) $x = 1.0$, and (d) $x = 1.5$.

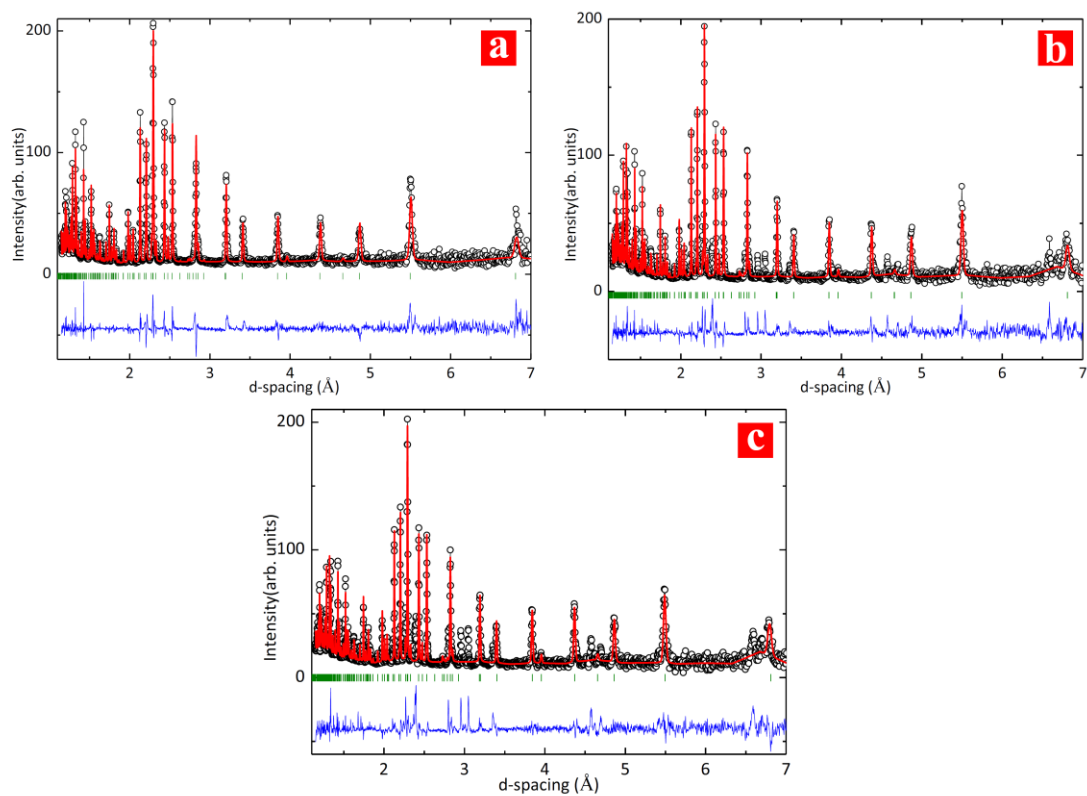


Figure S3. Neutron room temperature refinements from the POWGEN beamline at SNS using the $\lambda = 2.665$ Å bank for $\text{Sr}_{1.98-x}(\text{Ca}_{0.55}\text{Ba}_{0.45})_x\text{Si}_5\text{N}_8:\text{Eu}_{0.02}$ (a) $x = 0$, (b) $x = 1.0$, and (c) $x = 1.5$.

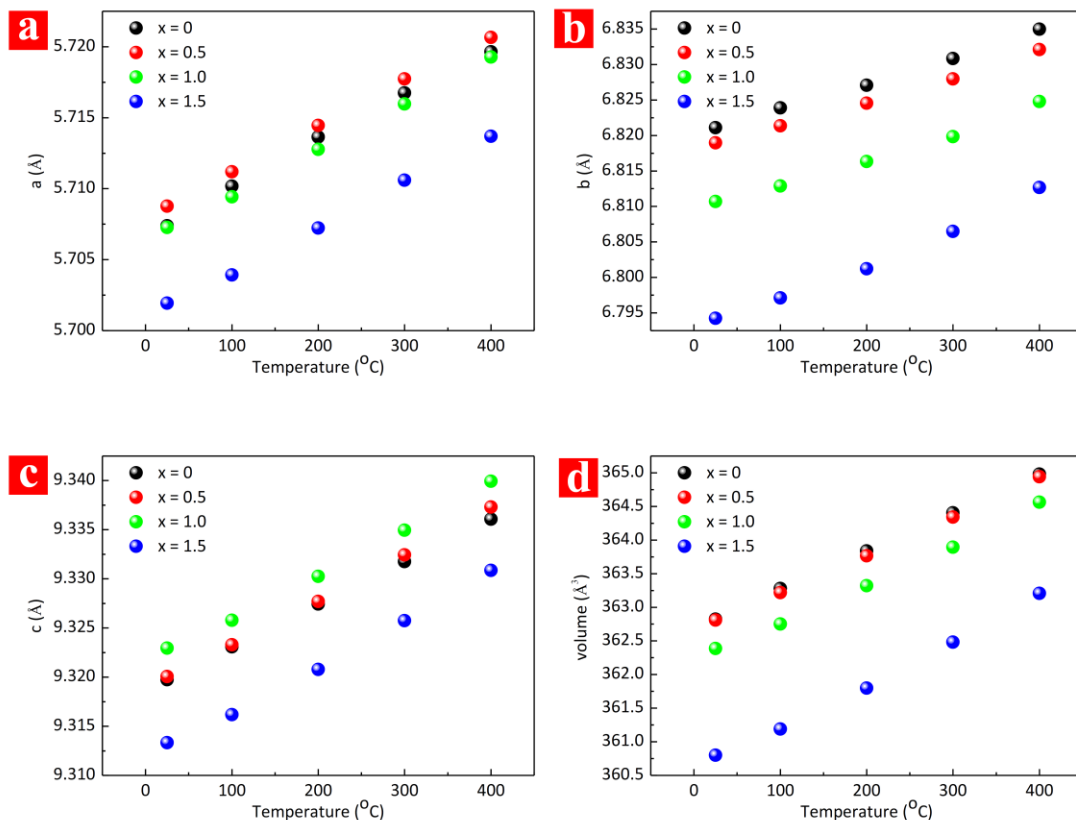


Figure S4. Variation of lattice parameters obtained from neutron diffraction with temperature for $\text{Sr}_{1.98-x}(\text{Ca}_{0.55}\text{Ba}_{0.45})_x\text{Si}_5\text{N}_8:\text{Eu}_{0.02}$ with $x = 0, 0.5, 1.0, 1.5$.

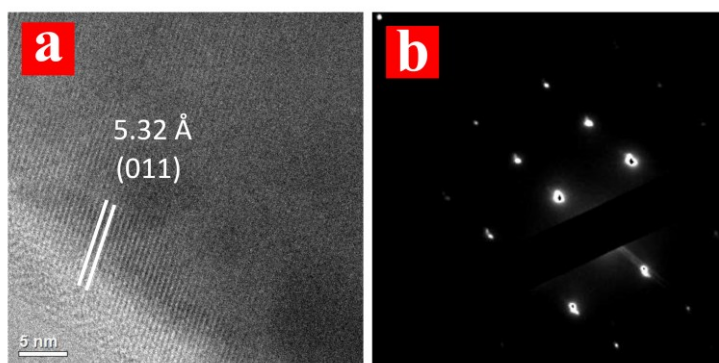


Figure S5. (a) High-resolution transmission electron microscopy (HRTEM) image for a typical crystallite of the $x = 0$ sample showing high uniform crystallinity. The indicated d-spacing of 5.32 Å is indexed on the (011) plane. (b) Selected area electron diffraction (SAED) pattern, which indicates high uniform crystallinity.

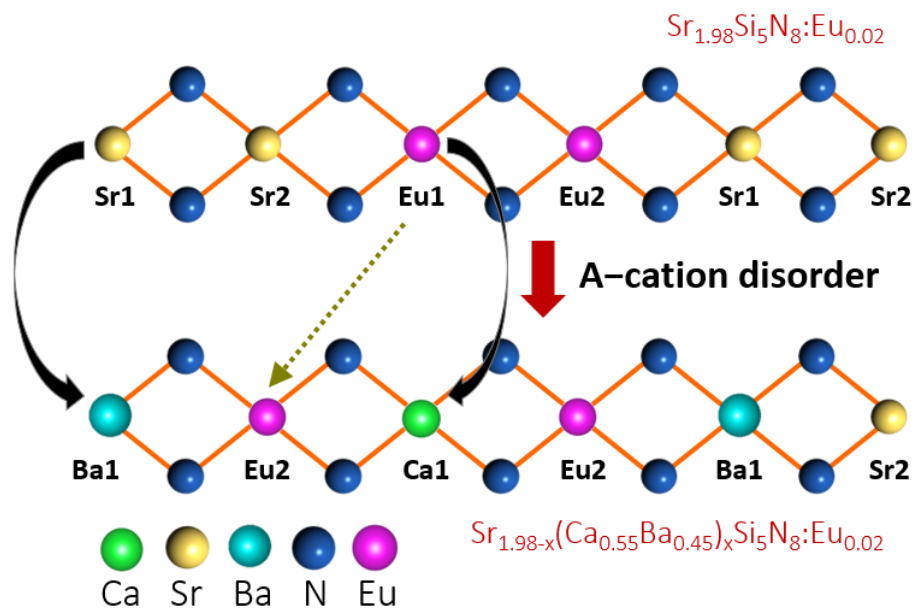


Figure S6. Schematic changes in local cation distributions driven by the A-cation disorder effect, where Eu^{2+} activators tend to migrate to Sr2 sites with increasing substitution of Ca and Ba with x , following the structure refinement results.

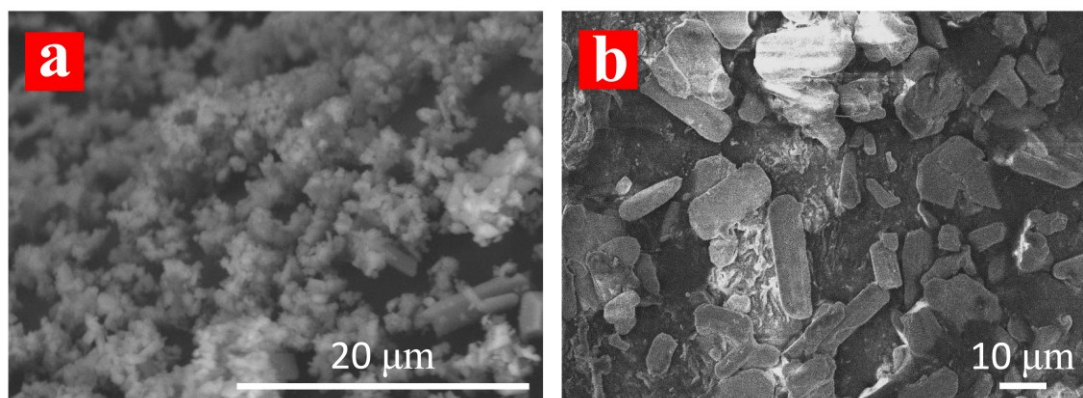


Figure S7. SEM images of nitridosilicate (a) $\text{Sr}_{0.48}(\text{Ca}_{0.55}\text{Ba}_{0.45})_{1.5}\text{Si}_5\text{N}_8:\text{Eu}_{0.02}$ and (b) commercial $\text{Sr}_{1.98}\text{Si}_5\text{N}_8:\text{Eu}_{0.02}$ phosphors, showing that larger particles are present in the commercial sample.

REFERENCES

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- (2) Gai, S.; Li, C.; Yang, P.; Lin, J. *Chem. Rev.* **2014**, *114*, 2343–2389.