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Electronic Supplementary Information

Controllable Eu Valence for Photoluminescence Tuing in Apatite-Typed Phosphors by Cation Cosubstitution Effect

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Experimental Section

***Synthsis*:** Oxyapatite solid solution compounds, $Ca_{0.98(2+x)}La_{0.98(8-x)}Eu_{0.2}(SiO_4)_{6-x}(PO_4)_xO_2$ (CLSPO; $x = 0$, 1, 2, 3, 4, 5, 6), were prepared using a high-temperature solid-state reaction process from stoichiometric mixing of $CaCO_3$ (Aldrich, ≥ 99.95%), La_2O_3 (Aldrich, ≥ 99.999%), SiO_2 (Aldrich, ≥ 99.995%), $(NH_4)_2HPO_4$ (Aldrich, ≥ 99.9%), and Eu_2O_3 (Aldrich, ≥ 99.999%) powders. The precursors were then ground in an agate mortar for 1 h with a small amount of absolute ethyl alcohol to form a homogeneous mixture. Afterward, the mixture powders were placed in aluminum oxide crucibles and fired at 1250 °C–1350 °C for 6 h under flowing 92% N_2–8% H_2 atmosphere in a horizontal tube furnace. After the furnace slowly cooled to room temperature, the sintered products were ground again, generating the final phosphor powders. The samples $Ca_{0.98(2+x)}La_{0.98(8-x)}Eu_{0.2}(SiO_4)_{6-x}(PO_4)_xO_2$ (CLSPO; $x = 0$, 1, 2, 3, 4, 5, 6) sintered at 1250 °C and 1350 °C were denoted by CLSPO-1250-0, 1, 2, 3, 4, 5, and 6 and CLSPO-1350-0, 1, 2, 3, 4, 5, and 6, respectively. Phosphor-converted solid-state lighting devices were fabricated around discrete UV LEDs by using gold wires for electrical operation. The LEDs emit with λ_{max} = 393 nm. Homogeneous mixtures of the as-prepared phosphors and transparent silicone resin were cured on the LED chip. After the packaging was completed, the optical properties of the device were measured in an integrating sphere under forward DC bias conditions.

***Characterization*:** Finely ground powders were used in all the measurements and analyses. Powder XRD measurements were performed on a D8 Focus diffractometer at a scanning rate of 10° min^{-1} in the 2θ range from 10° to 120°, with graphite-monochromatized Cu K_α radiation (λ = 0.15405 nm). XRD Rietveld profile refinements of the structural models and texture analysis were performed with the use of General Structure Analysis System. Photoluminescence measurements were recorded using a Fluoromax-4P spectrophotometer (Horiba Jobin Yvon, New Jersey, USA) equipped with a 450 W xenon lamp as excitation source. Both excitation and emission spectra were recorded with 1.0 nm interval with the width of monochromator slits adjusted to 0.50 nm. XANES of Eu L_3 edge was recorded with a wiggler beamline BL17C at National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. The thermal stability of the luminescence of these phosphor materials were measured by a Fluoromax-4P spectrometer connected to a heating equipment (TAP-02), and the samples were heated from 25°C to 250°C with a 25°C interval. After being remained at the designed temperature for two minutes, their emission spectra were recorded. PL decay curves were obtained from a Lecroy Wave Runner 6100 Digital Oscilloscope (1 GHz) by using a tunable laser (pulse width = 4 ns, gate = 50 ns) as excitation (Continuum Sunlite OPO). The Commission Internationale de l'Eclairage chromaticity color coordinates, color rendering index (R_a), and CCT of WLED devices were measured by Starspec SSP6612.

Table S1. The refined structure parameters of CLSPO-1250 (x = 0, 1, 2, 3, 4, 5, and 6) samples derived from the GSAS refinement of X-ray diffraction data.

Samples	$a = b$, Å	c, Å	V, Å^3	R_{wp}, %	R_p, %	χ^2
$x = 0$	9.64430(6)	7.13905(5)	575.059(6)	4.42	3.05	1.990
$x = 1$	9.61759(17)	7.10638(15)	569.261(19)	4.02	2.78	1.545
$x = 2$	9.59004(20)	7.07947(17)	563.861(22)	5.21	3.49	2.724
$x = 3$	9.5644(4)	7.05184(29)	558.66(4)	6.13	3.89	3.696
$x = 4$	9.5233(8)	7.0067(6)	550.32(8)	7.14	4.55	5.448
$x = 5$	9.4877(6)	6.9582(5)	542.44(6)	6.60	4.23	4.868
$x = 6$	9.45969(6)	6.92043(6)	536.312(7)	6.89	4.02	5.300
Space group: $P63/m$ (176), $\alpha = \beta = 90^o$, $\gamma = 120^o$						

Table S2. Selected interatomic distances of CLSPO-1250-6 and CLSPO-1350-6 samples.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
CLSPO-1250-6					
La1_O1	2.46515(1)	Ca1_O1	2.46090(1)	Ca2_O1	2.68448(1)
La1_O1	2.46452(1)	Ca1_O1	2.46027(1)	Ca2_O2	2.64255(1)
La1_O1	2.46463(1)	Ca1_O1	2.46037(1)	Ca2_O3	0.53141(0)
La1_O2	2.52222(1)	Ca1_O2	2.52641(1)	Ca2_O3	2.94369(1)
La1_O2	2.52259(1)	Ca1_O2	2.52678(1)	Ca2_O3	2.73908(1)
La1_O2	2.52190(1)	Ca1_O2	2.52609(1)	Ca2_O3	2.94369(1)
La1_O3	2.78474(1)	Ca1_O3	2.78355(1)	Ca2_O4	2.73908(1)
La1_O3	2.78443(1)	Ca1_O3	2.78325(1)		
La1_O3	2.78383(1)	Ca1_O3	2.78264(1)		
Average	2.590	**Average**	2.590	**Average**	2.474
CLSPO-1350-6					
La1_O1	2.44865(1)	Ca1_O1	2.43283(1)	Ca2_O1	1.73350(1)
La1_O1	2.44802(1)	Ca1_O1	2.43220(1)	Ca2_O2	3.10728(2)
La1_O1	2.44814(1)	Ca1_O1	2.43232(1)	Ca2_O3	2.32808(1)
La1_O2	2.43823(1)	Ca1_O2	2.45407(1)	Ca2_O3	2.48719(2)
La1_O2	2.43857(1)	Ca1_O2	2.45441(1)	Ca2_O3	2.32808(1)
La1_O2	2.43790(1)	Ca1_O2	2.45374(1)	Ca2_O3	2.48719(2)
La1_O3	2.79735(2)	Ca1_O3	2.79309(2)	Ca2_O4	2.84325(2)
La1_O3	2.79705(2)	Ca1_O3	2.79279(2)		
La1_O3	2.79644(2)	Ca1_O3	2.79218(2)		
Average	2.561	**Average**	2.560	**Average**	2.461

Table S3. CIE color coordinates, quantum yield (QYs) and emission positions of $Ca_{0.98(2+x)}La_{0.98(8-x)}Eu_{0.2}(SiO_4)_{6-x}(PO_4)_xO_2$ ($0 \leq x \leq 6$) prepared at 1250 ^{o}C (CLSPO-1250) and 1350 ^{o}C (CLSPO-1350), respectively (λ_{ex} = 393 nm).

CLSPO-1250/1350-*x* (0 ≤ *x* ≤ 6)	**CIE *x***	**CIE *y***	**Peak (nm)**	**Quantum Yield (QYs)**
CLSPO-1250				
x = 0	0.544	0.352	613	48.4%
x = 1	0.539	0.349	613	46.2%
x = 2	0.489	0.342	613	45.5%
x = 3	0.467	0.337	613	42.8%
x = 4	0.385	0.327	613	39.1%
x = 5	0.295	0.311	613	43.4%
x = 6	0.201	0.294	467	37.3%
CLSPO-1350				
x = 0	0.556	0.345	613	49.8%
x = 1	0.507	0.365	613	47.1%
x = 2	0.454	0.387	613	43.4%
x = 3	0.325	0.440	613	44.5%
x = 4	0.284	0.456	513	38.0%
x = 5	0.253	0.466	514	36.6%
x = 6	0.242	0.474	520	34.2%

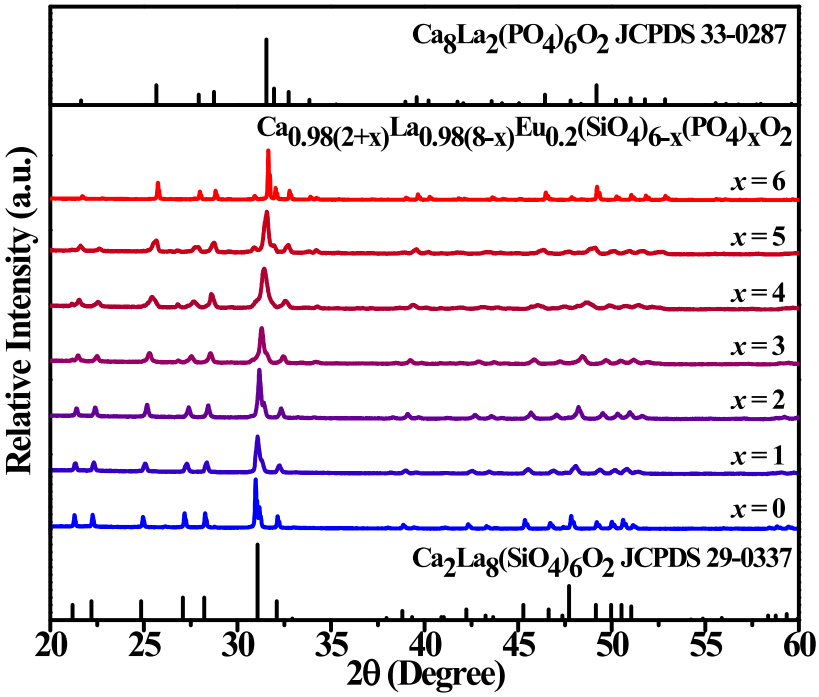

Fig. S1 (a) XRD patterns of the $Ca_{0.98(2+x)}La_{0.98(8-x)}Eu_{0.2}(SiO_4)_{6-x}(PO_4)_xO_2$ ($0 \leq x \leq 6$) samples. The standard JCPDS files of $Ca_2La_8(SiO_4)_6O_2$ (CLSO, No.29–0337) and $Ca_8La_2(PO_4)_6O_2$ (CLPO, No.33–0287) are used as references.

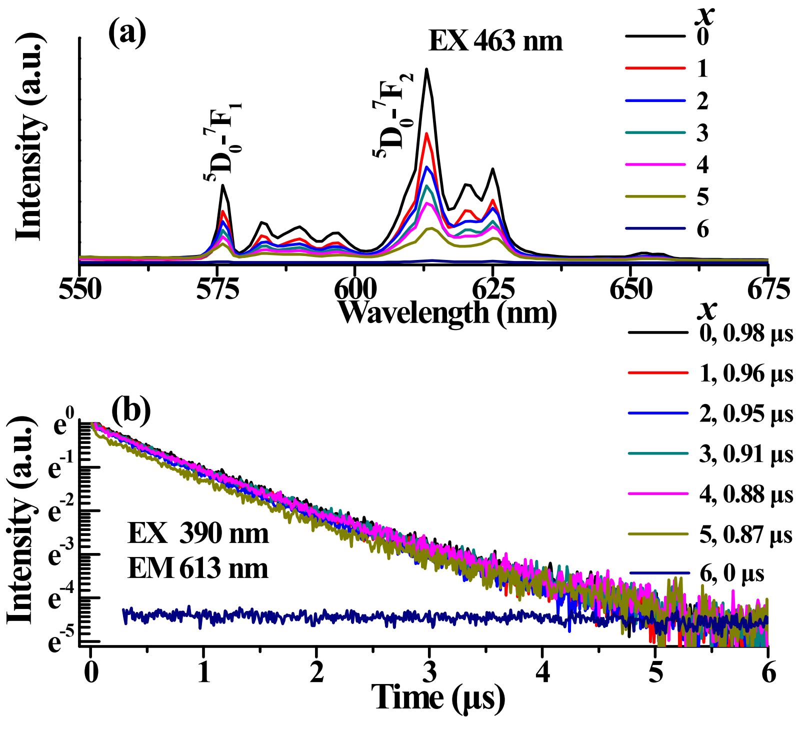

Fig. S2 (a) The PL spectra of the CLSPO-1250 samples monitoring with 463 nm blue light. (b) The decay curves of the CLSPO-1250 samples (λ_{ex} = 390 nm, λ_{em} = 613 nm).

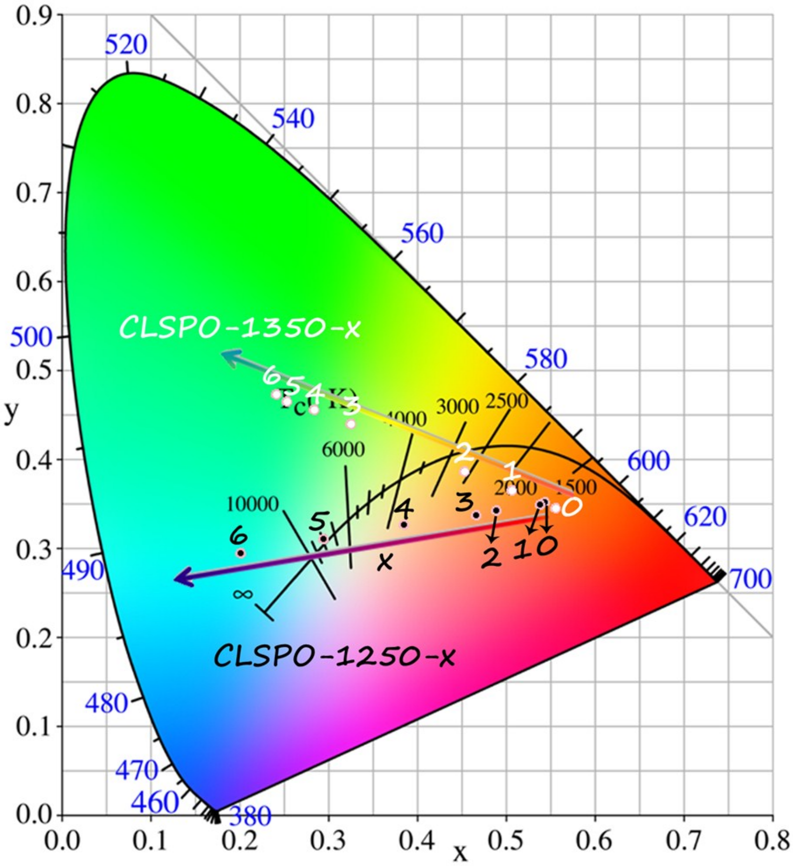

Fig. S3 CIE diagram of CLSPO-1250 and CLSPO-1350 ($0 \le x \le 6$) samples (λ_{ex} = 393 nm).

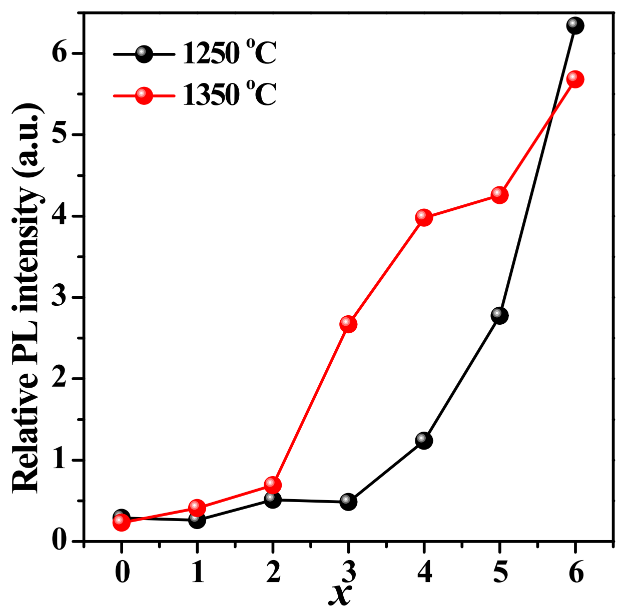

Fig. S4 Dependence of the photoluminescence emission intensity ratio of Eu^{2+}/Eu^{3+} on the amount of $[Ca^{2+}–P^{5+}]$ (x) incorporation in $Ca_{0.98(2+x)}La_{0.98(8-x)}Eu_{0.2}(SiO_4)_{6-x}(PO_4)_xO_2$ ($0 \le x \le 6$).

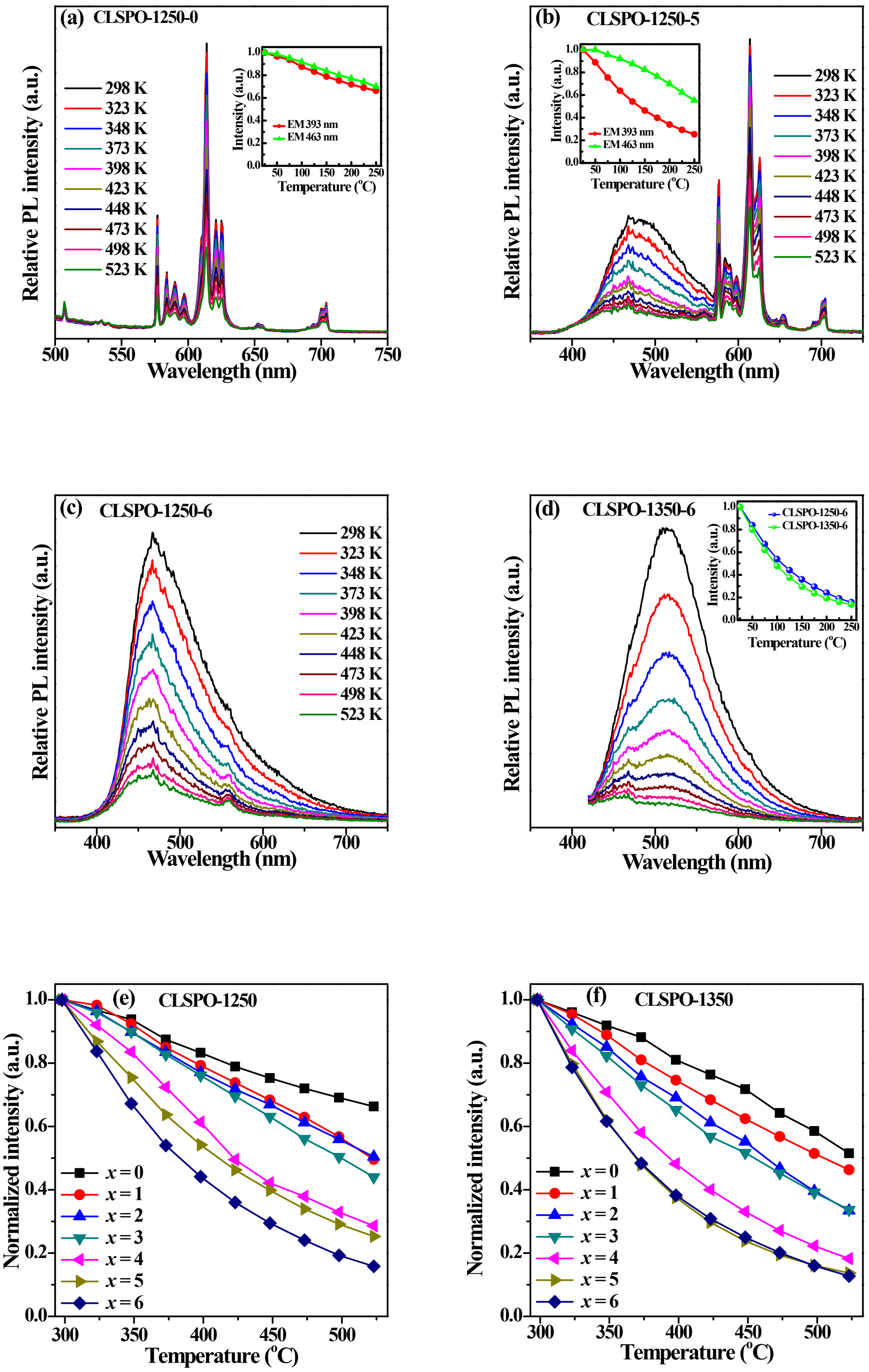

Fig. S5 PL spectra of $Ca_{0.98(2+x)}La_{0.98(8-x)}Eu_{0.2}(SiO_4)_{6-x}(PO_4)_xO_2$ ($0 \leq x \leq 6$) samples at different temperature (25-250 °C). (a) CLSPO-1250-0 (λ_{ex} = 463 nm), (b) CLSPO-1250-5 (λ_{ex} = 393 nm), (c) CLSPO-1250-6 (λ_{ex} = 393 nm), and (d) CLSPO-1350-6 (λ_{ex} = 393 nm). (e) and (f) are the dependence of emission intensity of CLSPO-1250 and CLSPO-1350 samples on temperatures (25-250 °C). The inserts in (a), (b), and (d) are also the dependence of emission intensity on temperatures (λ_{ex} = 393 nm).