Novel Yellowish-green Emitting $Ca_{10}(PO_4)_6O:Ce^{3+}$ Phosphor: Structural Refinement, Preferential Site Occupancy and Color Tuning

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EXPERIMENTAL SECTION

Chemicals and Materials. $CaCO_3$ (≥99.99%), CeO_2 (≥99.999%), and $CaHPO_4$ (≥99.9%) were purchased from Sigma-Aldrich Corporation. All of the initial chemicals were used without further purification. Aluminum oxide crucibles were used to sinter the phosphor samples.

Preparation. A series of $Ca_{10(1-x)}Ce_{10x}(PO_4)_6O$ (CPO:*x*Ce) (x = 0–0.30) compounds were prepared by a conventional high-temperature solid state reaction. Stoichiometric amounts of $CaCO_3$, CeO_2 and $CaHPO_4$ were thoroughly mixed and pestled in an agate mortar for 1 h. Then, the powder mixtures were placed in aluminum oxides crucibles and sintered in a horizontal tube furnace at 1250°C for 8 h with a reducing atmosphere of H_2 (8%) and N_2 (92%) atmosphere. After the furnace slowly cooled to room temperature, the sintered products were grinded again, generating the final phosphor powders.

Characterization. Finely ground powders were used in all of the measurements. The phase purity of all samples were analyzed using X-ray diffraction (XRD) obtained in a D8 Focus diffractometer (Bruker, Kalsruhe, Germany) at a scanning rate of 1° min^{-1} in the 2θ range from 5° to 120°, and the counting time was 5 s per step with Ni-filtered Cu Kα radiation (λ = 0.15406 nm). XRD Rietveld profile refinements of the structural models and texture analysis were performed with the use of General Structure Analysis System (GSAS). The starting model was built with crystallographic data taken from $Ca_{10}(PO_4)_6S$. [*J. Solid State Chem.*, 1986, **63**, 267–277.] The element contents of Ca, Ce and P were measured by inductively coupled plasma (ICP) optical emission spectrometer (ICP-OES, ICAP 6300, Thermal Scientific). The photoluminescence measurements were recorded with a Fluoromax-4P spectrophotometer (Horiba Jobin Yvon, New Jersey, U.S.A.) equipped with a 450 W xenon lamp as the excitation source. Both excitation and emission spectra were set up to be 1.0 nm with the width of the monochromator slits adjusted as 0.50 nm. The absorption spectra were measured by UV-Visible diffuse reflectance spectroscopy UV-2550PC (Shimadzu Corporation, Japan). The thermal stability of luminescence of phosphor materials were measured by Fluoromax-4P spectrometer connected a heating equipment (TAP-02). The luminescence decay curves were obtained from a Lecroy Wave Runner 6100 digital oscilloscope (1 GHz) using a tunable laser (pulse width= 4 ns, gate= 50 ns) as excitation source (Continuum Sunlite OPO). The photoluminescence quantum yields (QYs) were measured by absolute PL quantum yield measurement system C9920-02 (Hamamatsu photonics K.K., Japan). All the measurements were performed at room temperature (RT).

Table S1. Final refined structure parameters of $Ca_{10}(PO_4)_6O$ and $Ca_8Ce_2(PO_4)_6O$ derived from the GSAS refinement of X-ray diffraction data.

Atom	Wyckoff position	X	Y	Z	Frac.	Uiso
			$Ca_{10}(PO_4)_6O$			
Ca1	2b	0.3333000(0)	0.6667000(0)	0.0254220(0)	0.842(0)	0.01481
Ca2	2b	0.6667000(0)	0.3333000(0)	0.0217650(0)	1.005(0)	0.09211
Ca3	6c	0.2448330(0)	-0.0098720(0)	0.2660860(0)	0.918(0)	0.05319
P	6c	0.3968560(0)	0.3679970(0)	0.2685350(0)	0.931(0)	0.04912
O1	6c	0.3285290(0)	0.4869290(0)	0.2798710(0)	0.953(0)	0.04268
O2	6c	0.5853260(0)	0.4668090(0)	0.2555540(0)	0.935(0)	0.05787
O3	6c	0.3499700(0)	0.2650280(0)	0.0671630(0)	0.792(0)	0.03299
O4	6c	-0.3266020(0)	-0.2422670(0)	-0.0701070(0)	1.118(0)	0.09997
O5	2a	0.0000000(0)	0.0000000(0)	0.3374(16)	0.455(5)	0.10234
Cell parameters: $a = b = 9.40521(6)$ $c = 6.88127(5)$ Å, $\alpha = \beta = 90^o$, $\gamma = 120^o$, $V = 527.152(6)$ Å^3, $z = 1$ Space group: $P6_{3/m}$ (173) Reliability factor: $R_{wp} = 4.89\%$, $R_p = 3.25\%$, and $\chi^2 = 2.658$						
			$Ca_8Ce_2(PO_4)_6O$			
Ca1/Ce1	2b	0.3333000(0)	0.6667000(0)	0.0308730(0)	0.876(0)	0.02603
Ca2/Ce1	2b	0.6667000(0)	0.3333000(0)	0.0402440(0)	0.672(0)	0.06452
Ca3/Ce1	6c	0.2213720(0)	-0.0134950(0)	0.2849820(0)	1.238(0)	0.03780
P	6c	0.4021730(0)	0.3762960(0)	0.2706450(0)	0.830(0)	0.04348
O1	6c	0.3272560(0)	0.4841880(0)	0.2532260(0)	1.129(0)	0.09095
O2	6c	0.5903200(0)	0.4647740(0)	0.2591320(0)	0.728(0)	0.02920
O3	6c	0.3776760(0)	0.2872200(0)	0.0985140(0)	0.606(0)	0.02235
O4	6c	-0.3182730(0)	-0.2505710(0)	-0.0542980(0)	1.168(0)	0.07892
O5	2a	0.0000000(0)	0.0000000(0)	0.282(5)	0.503(8)	0.20388
Cell parameters: $a = b = 9.43671(8)$ Å, $c = 6.91143(6)$ Å, $\alpha = \beta = 90^o$, $\gamma = 120^o$, $V = 533.016(8)$ Å^3, $z = 1$ Space group: $P6_{3/m}$ (173) Reliability factor: $R_{wp} = 3.93\%$, $R_p = 2.70\%$, and $\chi^2 = 1.864$						

Table S2. Selected interatomic distances in $Ca_8Ce_2(PO_4)_6O$

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Ca1/Ce1-O1	2.28759(1)	Ca2/Ce2-O1	2.60831(2)	Ca3/Ce3-O1	2.71739(2)
Ca1/Ce1-O1	2.28726(1)	Ca2/Ce2-O1	2.60892(2)	Ca3/Ce3-O2	2.57670(2)
Ca1/Ce1-O1	2.28689(1)	Ca2/Ce2-O1	2.60863(2)	Ca3/Ce3-O3	2.77556(2)
Ca1/Ce1-O2	2.54507(2)	Ca2/Ce2-O2	2.28948(1)	Ca3/Ce3-O3	2.46182(2)
Ca1/Ce1-O2	2.54566(2)	Ca2/Ce2-O2	2.28893(1)	Ca3/Ce3-O4	2.44482(2)
Ca1/Ce1-O2	2.54516(2)	Ca2/Ce2-O2	2.28882(1)	Ca3/Ce3-O4	2.44970(2)
Ca1/Ce1-O4	3.03316(2)	Ca2/Ce2-O3	2.56986(2)	Ca3/Ce3-O5	2.15561(33)
Ca1/Ce1-O4	3.03226(2)	Ca2/Ce2-O3	2.56894(2)	————	————
Ca1/Ce1-O4	3.03289(2)	Ca2/Ce2-O3	2.56952(2)	————	————
Average Ca1/Ce1-O	2.622	Average Ca2/Ce2-O	2.459	Average Ca3/Ce3-O	2.512

Table S3. Main parameters of processing and refinement of the $Ca_{10(1-x)}Ce_{10x}(PO_4)_6O$ (x = 0–0.30) samples

x	Space group	Cell parameters, Å	Cell volume, Å^3	R_{wp}, R_p, %, χ^2
0	$P6_{3/m}$ (173)	$a = b$ = 9.40521(6) c = 6.88127(5) α = β = 90° γ = 120°	527.152(6)	4.89, 3.25, 2.658
0.05	$P6_{3/m}$ (173)	$a = b$ = 9.41643(9) c = 6.88637(7) α = β = 90° γ = 120°	528.803(9)	4.49, 2.97, 2.360
0.10	$P6_{3/m}$ (173)	$a = b$ =9.42338(12) c = 6.89633(10) α = β = 90° γ = 120°	530.349(12)	5.16, 3.28, 2.999
0.15	$P6_{3/m}$ (173)	$a = b$ = 9.42970(9) c = 6.90614(8) α = β = 90° γ = 120°	531.816(9)	5.29, 3.35, 3.140
0.20	$P6_{3/m}$ (173)	$a = b$ = 9.43671(8) c = 6.91143(6) α = β = 90° γ = 120°	533.016(8)	3.93, 2.70, 1.864
0.25	$P6_{3/m}$ (173)	$a = b$ = 9.44121(8) c = 6.91523(7) α = β = 90° γ = 120°	533.817(8)	4.15, 2.87, 2.095
0.30	$P6_{3/m}$ (173)	$a = b$ = 9.44226(9) c = 6.91596(8) α = β = 90° γ = 120°	533.992(10)	6.23, 3.87, 4.489

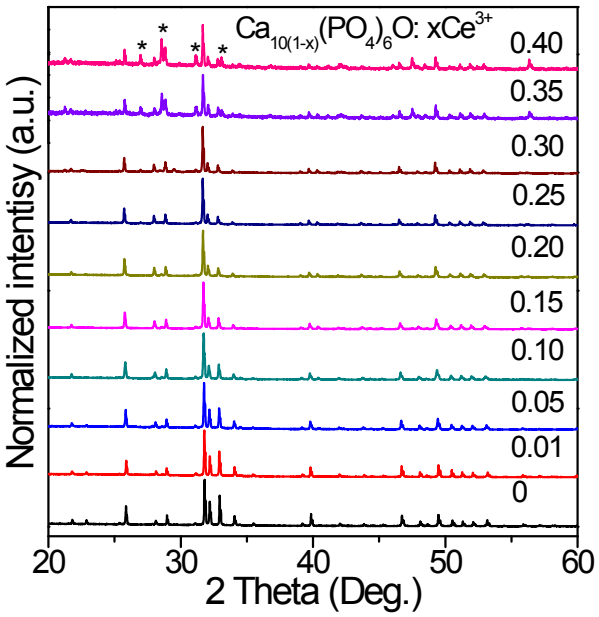

Figure S1. The XRD patterns at 2θ = 20°–60° of $Ca_{10(1-x)}Ce_{10x}(PO_4)_6O$ (x = 0–0.40) samples.

Table S4. The ICP analysis of Ca, Ce and P contents in some representative $Ca_{10(1-x)}Ce_{10x}(PO_4)_6O$ (x = 0–0.15) samples.

$Ca_{10(1-x)}Ce_{10x}(PO_4)_6O$	Element content (ppm)			(Ca+Ca)/P	Ce/Ca
	Ca	Ce	P		
$x = 0$	411000	0	193700	1.640	0
$x = 0.03$	275200	57750	182200	1.660	0.04403
$x = 0.05$	327600	119900	169900	1.646	0.10469
$x = 0.10$	269900	230800	157100	1.653	0.2446
$x = 0.15$	212500	274800	138900	1.620	0.36989

Table S5. CIE color coordinates, emission peaks, quantum efficiencies (QEs) and FWHM of $Ca_{10(1-x)}Ce_{10x}(PO_4)_6O$ (x = 0–0.30) samples excited under different UV (330-355 nm).

CPO: x Ce^{3+}	CIE color coordinates (X, Y)	Emission peak / nm	QEs	FWHM / nm
1%	(0.165, 0.056)	415	0.186	58
5%	(0.178, 0.161)	421	0.192	93
10%	(0.186, 0.199)	448	0.246	107
15%	(0.198, 0.250)	466	0.305	126
20%	(0.226, 0.304)	480	0.268	142
25%	(0.262, 0.394)	498	0.227	142
30%	(0.298, 0.434)	510	0.212	136

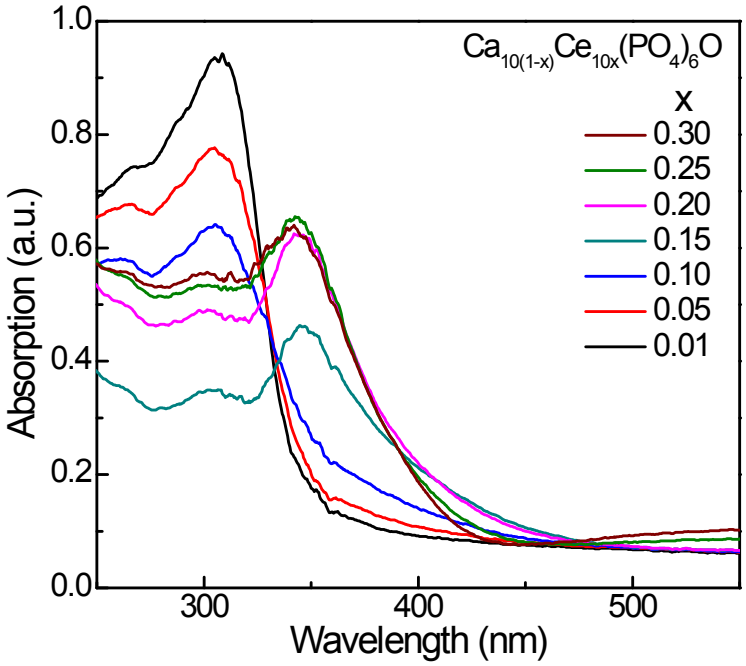

Figure S2. The absorption spectra of $Ca_{10(1-x)}Ce_{10x}(PO_4)_6O$ (x = 0–0.30) samples.

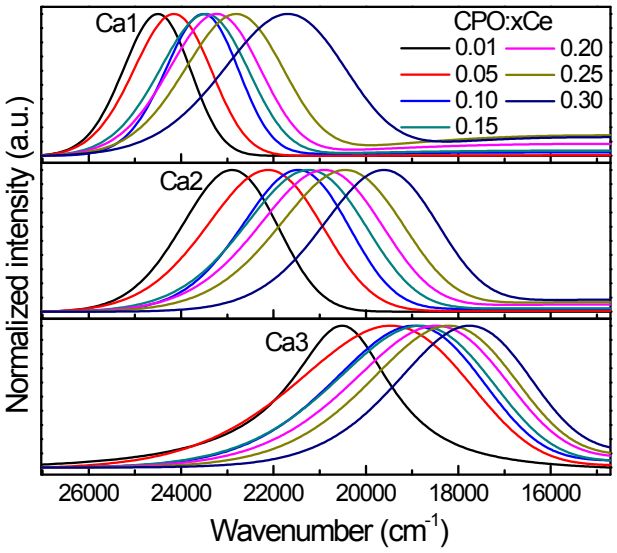

Figure S3. Normalized Gaussian fitting PL spectra of $Ca_{10(1-x)}Ce_{10x}(PO_4)_6O$ (x = 0–0.30) samples at three Ca^{2+} sites.

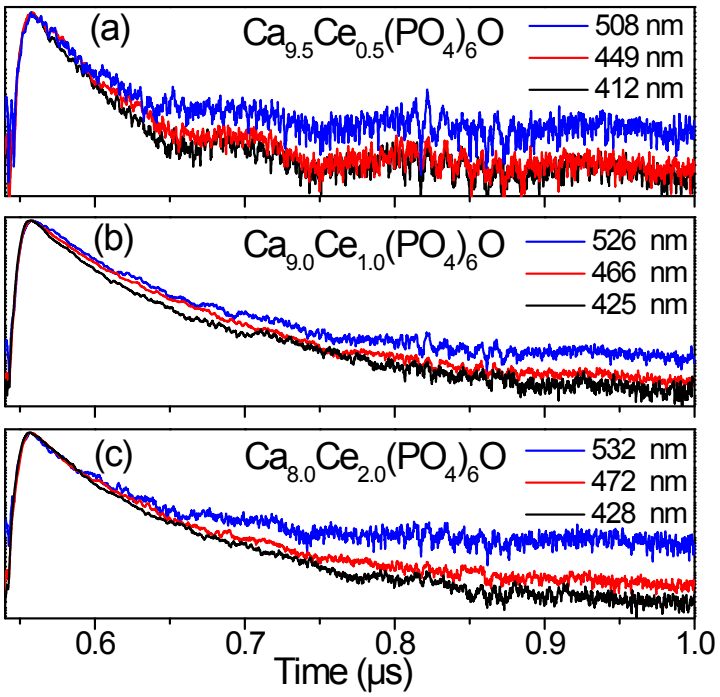

Figure S4. The lifetime decay curves of the representative $Ca_{10(1-x)}Ce_{10x}(PO_4)_6O$ (x = 0.05, 0.10, 0.20) samples excited at different Ca^{2+} sites.

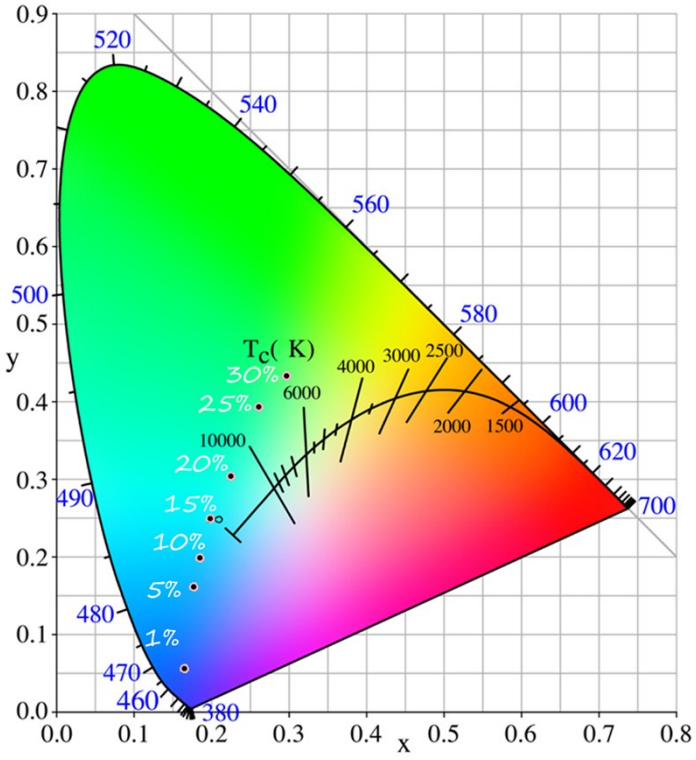

Figure S5. CIE color coordinates diagram of $Ca_{10(1-x)}Ce_{10x}(PO_4)_6O$ (x = 0–0.30) samples excited under different UV (330-355 nm).