Electronic Supplementary Information (ESI)

Multichannel photoluminescence tuning in Eu-doped apatite phosphors via coexisting cation substitution, energy transfer and valence mixing

Peipei Dang,[a,c] Guogang Li,*[,b] Sisi Liang,[a,c] Hongzhou Lian,[a] and Jun Lin*[a,c,d]

[a] *State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China. E-mail: jlin@ciac.ac.cn*

[b] *Engineering Research Center of Nano-Geomaterials of Ministry of Education, Faculty of Materials Science and Chemistry, China University of Geosciences, 388 Lumo Road, Wuhan 430074, P. R. China. E-mail: ggli@cug.edu.cn*

[c] *University of Science and Technology of China, Hefei, 230026, P. R. China*

[d] *School of Applied Physics and Materials, Wuyi University, Jiangmen, Guangdong 529020, P. R. China*

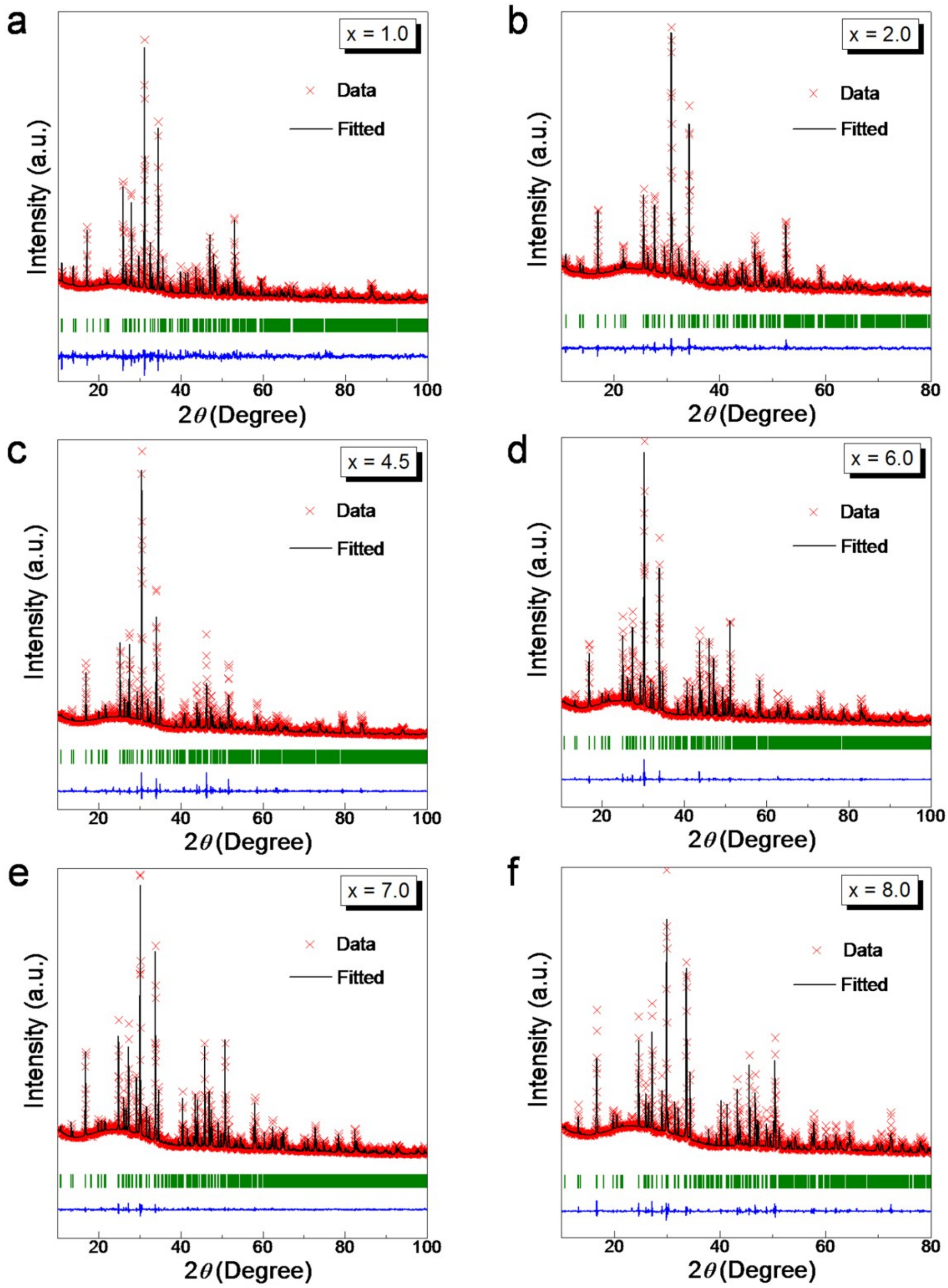

Figure S1. Data (red dots) and fitted (black line) powder XRD patterns as well as difference profile (blue line) for Rietveld analysis of $Ca_{8.97-x}Sr_xLiGd_{2/3}(PO_4)_7$:$0.03Eu^{2+}$: (a) x = 1.0, (b) x = 2.0, (c) x = 4.5, (d) x = 6.0, (e) x = 7.0, (f) x = 8.0.

Table S1. Main refinement parameters of the $Ca_{8.97-x}Sr_xLiGd_{2/3}(PO_4)_7$:$0.03Eu^{2+}$ (x = 0-9.0) samples.

Space group: $R3c$ (161), $Z = 6$			
x	Cell parameters, Å	Cell volume, Å^3	R_{wp}, R_p, %, χ^2
$x = 0$	$a = b = 10.4198$ $c = 37.3065$ $\alpha = \beta = 90^{o}$ $\gamma = 120°$	3507.79	3.32, 2.54, 2.021
$x = 1.0$	$a = b = 10.4638$ $c = 37.5072$ $\alpha = \beta = 90^{o}$ $\gamma = 120°$	3556.53	3.87, 2.90, 2.976
$x = 2.0$	$a = b = 10.5001$ $c = 37.7534$ $\alpha = \beta = 90^{o}$ $\gamma = 120°$	3604.75	3.58, 2.69, 2.697
$x = 3.0$	$a = b = 10.5200$ $c = 38.0328$ $\alpha = \beta = 90^{o}$ $\gamma = 120°$	3645.21	5.46, 3.74, 6.152
$x = 4.5$	$a = b = 10.5589$ $c = 38.4480$ $\alpha = \beta = 90^{o}$ $\gamma = 120°$	3712.03	5.86, 3.89, 7.092
$x = 6.0$	$a = b = 10.6004$ $c = 38.8463$ $\alpha = \beta = 90^{o}$ $\gamma = 120°$	3780.30	4.41, 3.03, 4.167
$x = 7.0$	$a = b = 10.6325$ $c = 39.0975$ $\alpha = \beta = 90^{o}$ $\gamma = 120°$	3827.84	4.06, 2.95, 3.556
$x = 8.0$	$a = b = 10.6652$ $c = 39.3180$ $\alpha = \beta = 90^{o}$ $\gamma = 120°$	3873.11	5.89, 4.01, 8.463
$x = 9.0$	$a = b = 10.7052$ $c = 39.6157$	3931.74	5.75, 3.92, 7.491

	$\alpha = \beta = 90^{o}$ $\gamma = 120°$

Table S2. Final refined structure parameters of $Ca_{8.97-x}Sr_xLiGd_{2/3}(PO_4)_7$:$0.03Eu^{2+}$ (x = 0, 4.5, 9.0) samples derived from the GSAS refinement of XRD data.

Atom	Wyckoff	X	Y	Z	Frac.	*Uiso*
			$x = 0$			
Ca1	18b	0.719800	0.853300	0.431700	1.1624	0.40(26)
Ca2	18b	0.610965	0.817987	0.232102	1.4189	1.04(25)
Ca3	18b	0.132627	0.275344	0.325060	1.1375	0.72(26)
Gd1/Li1	6a	0	0	0	0.3855	0.03
P1	6a	0	0	0.154559	3.7384	80
P2	18b	0.683944	0.863842	0.129928	1.0022	-1.67
P3	18b	0.653600	0.845400	0.031400	1.0000	2.53
O1	6a	0	0	0.404033	1.0000	3.78
O2	18b	0.017900	0.866200	0.254900	3.1308	55.72
O3	18b	0.716367	0.892606	0.191529	1.6965	14.58
O4	18b	0.750017	0.769375	0.121693	1.0000	-4.70
O5	18b	0.698550	0.003771	0.102815	1.0000	-1.42
O6	18b	0.510800	0.764000	0.129100	1.0000	0.03
O7	18b	0.606300	0.953100	0.044600	1.0000	0.03
O8	18b	0.581300	0.692000	0.044900	1.0000	0.03
O9	18b	0.826100	0.920000	0.040000	1.0000	0.03
O10	18b	0.631400	0.822300	0.990800	1.0000	0.03

$x = 4.5$						
Ca1	18b	0.6959(9)	0.8240(14)	0.43225(26)	1.901(46)	4.70(42)
Ca2	18b	0.6262(8)	0.8267(16)	0.23115(23)	2.061(34)	5.09(34)
Ca3	18b	0.188526	0.379331	0.336778	1.5597	0.09
Gd1/Li1	6a	0	0	-0.002358	0.4663	3.04
P1	6a	0	0	0.243292	1.6669	23.18
P2	18b	0.707169	0.801546	0.130690	1.1901	2.67
P3	18b	0.646962	0.806482	0.030041	0.9114	0.00
O1	6a	0	0	0.296845	2.2176	46.29
O2	18b	0.438117	0.938522	0.318192	1.0000	80.00
O3	18b	0.778828	0.712435	0.157261	0.4355	5.21
O4	18b	0.518332	-0.520957	0.085396	-0.0817	-5.69
O5	18b	0.716536	-0.030611	0.120861	1.0000	0.03
O6	18b	0.532590	0.766879	0.126157	1.0000	7.21
O7	18b	0.606300	0.953100	0.044600	1.0000	0.03
O8	18b	0.579214	0.711526	0.053318	1.0000	0.03
O9	18b	0.836158	0.915515	0.039454	1.0000	0.03
O10	18b	0.578786	0.812025	0.999658	1.0000	0.03

			x = 9.0			
Sr1	18b	0.697956	0.849263	0.430677	1.2682	2.48
Sr2	18b	0.623342	0.818166	0.228706	1.4975	1.01
Sr3	18b	0.141347	0.295053	0.324498	1.2101	2.41
Gd1/Li1	6a	0	0	-0.001113	0.5623	2.29
P1	6a	0	0	0.279919	1.0000	32.55
P2	18b	0.674667	0.839910	0.130154	0.9418	0.67
P3	18b	0.877342	0.689475	-0.004513	0.8344	7.59
O1	6a	0	0	0.370148	3.0442	43.22
O2	18b	0.058615	0.884234	0.267436	1.0000	3.58
O3	18b	0.795536	0.858128	0.198055	2.6690	76.61
O4	18b	0.771007	0.787678	0.112879	0.8043	2.03
O5	18b	0.730700	0.003400	0.111900	1.2052	2.71
O6	18b	0.491672	0.778599	0.098125	1.1585	1.95
O7	18b	0.606300	0.953100	0.044600	1.0000	8.08
O8	18b	0.581300	0.692000	0.044900	1.0000	0.03
O9	18b	0.826100	0.920000	0.040000	1.0000	0.03
O10	18b	0.631400	0.822300	0.990800	1.0000	0.03

Table S3. Main bond lengths (Å) of $Ca_{8.97-x}Sr_xLiGd_{2/3}(PO_4)_7$:$0.03Eu^{2+}$ (x = 0-9.0) samples.

***x* = 0**					
Ca1-O1	2.73189(4)	Ca2-O2	2.35252(4)	Ca3-O2	2.92004(5)
Ca1-O2	2.45057(4)	Ca2-O3	1.80219(3)	Ca3-O3	3.03874(5)
Ca1-O4	2.79375(5)	Ca2-O4	2.49102(4)	Ca3-O4	2.46917(3)
Ca1-O5	2.18564(4)	Ca2-O5	2.19840(3)	Ca3-O5	2.67353(4)
Ca1-O6	2.45521(4)	Ca2-O7	2.62262(4)	Ca3-O7	2.42354(4)
Ca1-O6	2.53603(4)	Ca2-O8	2.75090(5)	Ca3-O8	2.45801(4)
Ca1-O7	2.45868(4)	Ca2-O9	2.40015(4)	Ca3-O10	2.58438(5)
Ca1-O8	2.46673(4)	Ca2-O9	2.38346(4)	Ca3-O10	2.60406(5)
Ca1-O10	2.34469(4)				
Average length (Å)	2.492	Average length (Å)	2.375	Average length (Å)	2.646
***x* = 1.0**					
Ca1/Sr1-O2	2.85767(3)	Ca2/Sr2-O2	2.47125(3)	Ca3/Sr3-O2	3.13469(3)
Ca1/Sr1-O4	2.79445(3)	Ca2/Sr2-O3	2.46871(3)	Ca3/Sr3-O3	2.88558(4)
Ca1/Sr1-O5	2.85816(4)	Ca2/Sr2-O4	2.62076(3)	Ca3/Sr3-O4	2.49912(3)
Ca1/Sr1-O6	2.58288(3)	Ca2/Sr2-O5	2.26010(2)	Ca3/Sr3-O5	2.40971(2)
Ca1/Sr1-O6	2.26528(3)	Ca2/Sr2-O7	2.47180(3)	Ca3/Sr3-O7	2.41046(2)
Ca1/Sr1-O7	2.59210(3)	Ca2/Sr2-O8	3.21185(4)	Ca3/Sr3-O8	2.38443(2)
Ca1/Sr1-O8	2.35462(2)	Ca2/Sr2-O9	2.22721(3)	Ca3/Sr3-O10	2.67495(4)
Ca1/Sr1-O10	2.47639(3)	Ca2/Sr2-O9	2.60399(3)	Ca3/Sr3-O10	2.57657(3)
Average length (Å)	2.598	Average length (Å)	2.542	Average length (Å)	2.622
***x* = 2.0**					
Ca1/Sr1-O2	2.574(11)	Ca2/Sr2-O2	3.170(13)	Ca3/Sr3-O1	2.67033(7)

Ca1/Sr1-O4	2.770(15)	Ca2/Sr2-O2	2.948(12)	Ca3/Sr3-O3	2.98255(7)
Ca1/Sr1-O5	2.650(16)	Ca2/Sr2-O3	2.353(12)	Ca3/Sr3-O4	2.51528(5)
Ca1/Sr1-O6	2.489(13)	Ca2/Sr2-O4	2.524(15)	Ca3/Sr3-O5	2.44994(5)
Ca1/Sr1-O6	2.494(14)	Ca2/Sr2-O5	2.251(16)	Ca3/Sr3-O7	2.42070(5)
Ca1/Sr1-O7	2.523(13)	Ca2/Sr2-O7	2.497(20)	Ca3/Sr3-O8	2.43994(5)
Ca1/Sr1-O8	2.447(12)	Ca2/Sr2-O8	2.888(20)	Ca3/Sr3-O10	2.66540(7)
Ca1/Sr1-O10	2.388(10)	Ca2/Sr2-O9	2.426(14)	Ca3/Sr3-O10	2.63589(7)
Average length (Å)	2.542	Average length (Å)	2.632	Average length (Å)	2.598
		x = 3.0			
Ca1/Sr1-O2	3.11628(7)	Ca2/Sr2-O2	1.08833(3)	Ca3/Sr3-O1	2.885(8)
Ca1/Sr1-O4	2.89093(6)	Ca2/Sr2-O4	3.12600(5)	Ca3/Sr3-O3	2.783(10)
Ca1/Sr1-O5	2.85572(7)	Ca2/Sr2-O5	2.31672(4)	Ca3/Sr3-O4	2.522(17)
Ca1/Sr1-O6	2.89433(6)	Ca2/Sr2-O7	2.48816(5)	Ca3/Sr3-O5	2.348(13)
Ca1/Sr1-O6	2.53723(5)	Ca2/Sr2-O8	2.97348(7)	Ca3/Sr3-O7	2.277(14)
Ca1/Sr1-O7	2.59393(4)	Ca2/Sr2-O9	2.39377(5)	Ca3/Sr3-O8	2.445(15)
Ca1/Sr1-O8	2.63049(4)	Ca2/Sr2-O9	2.58648(5)	Ca3/Sr3-O10	2.631(20)
Ca1/Sr1-O10	2.26170(4)			Ca3/Sr3-O10	2.788(20)
Average length (Å)	2.723	Average length (Å)	2.425	Average length (Å)	2.585
		x = 4.5			
Ca1/Sr1-O4	0.856(10)	Ca2/Sr2-O2	3.205(9)	Ca3/Sr3-O2	2.37195(9)
Ca1/Sr1-O5	2.829(14)	Ca2/Sr2-O4	3.131(13)	Ca3/Sr3-O2	2.95344(11)
Ca1/Sr1-O6	2.813(11)	Ca2/Sr2-O5	2.842(13)	Ca3/Sr3-O3	0.96520(3)
Ca1/Sr1-O6	2.526(11)	Ca2/Sr2-O7	2.631(15)	Ca3/Sr3-O4	3.15140(14)
Ca1/Sr1-O7	2.649(12)	Ca2/Sr2-O8	2.810(17)	Ca3/Sr3-O5	2.52870(8)
Ca1/Sr1-O8	2.368(11)	Ca2/Sr2-O9	2.618(11)	Ca3/Sr3-O7	2.26609(7)
Ca1/Sr1-O10	2.804(10)	Ca2/Sr2-O9	2.421(11)	Ca3/Sr3-O8	2.94182(9)
				Ca3/Sr3-O10	2.82324(11)

Average length (Å)	2.406	Average length (Å)	2.808	Average length (Å)	2.500
***x* = 6.0**					
Ca1/Sr1-O2	2.39170(3)	Ca2/Sr2-O2	1.90809(3)	Ca3/Sr3-O1	3.23882(4)
Ca1/Sr1-O4	3.06514(5)	Ca2/Sr2-O3	2.86681(4)	Ca3/Sr3-O2	2.87574(4)
Ca1/Sr1-O5	2.68420(5)	Ca2/Sr2-O4	2.44960(4)	Ca3/Sr3-O3	2.77845(5)
Ca1/Sr1-O6	2.69925(4)	Ca2/Sr2-O5	2.40484(3)	Ca3/Sr3-O4	2.38366(3)
Ca1/Sr1-O6	2.60562(4)	Ca2/Sr2-O7	2.45567(4)	Ca3/Sr3-O5	2.39823(3)
Ca1/Sr1-O7	2.60988(3)	Ca2/Sr2-O8	2.81347(5)	Ca3/Sr3-O7	2.84490(4)
Ca1/Sr1-O8	2.51465(3)	Ca2/Sr2-O9	2.36688(4)	Ca3/Sr3-O8	2.55736(3)
Ca1/Sr1-O10	2.34488(4)	Ca2/Sr2-O9	2.60915(4)	Ca3/Sr3-O10	2.60066(5)
				Ca3/Sr3-O10	2.77217(5)
Average length (Å)	2.614	Average length (Å)	2.484	Average length (Å)	2.717
***x* = 7.0**					
Ca1/Sr1-O2	2.39170(3)	Ca2-O2	1.90809(3)	Ca3/Sr3-O2	2.87574(4)
Ca1/Sr1-O4	3.06514(5)	Ca2-O3	2.86681(4)	Ca3/Sr3-O3	2.77845(5)
Ca1/Sr1-O5	2.68420(5)	Ca2-O4	2.44960(4)	Ca3/Sr3-O4	2.38366(3)
Ca1/Sr1-O6	2.69925(4)	Ca2-O5	2.40484(3)	Ca3/Sr3-O5	2.39823(3)
Ca1/Sr1-O6	2.60562(4)	Ca2-O7	2.45567(4)	Ca3/Sr3-O7	2.84490(4)
Ca1/Sr1-O7	2.60988(3)	Ca2-O8	2.81347(5)	Ca3/Sr3-O8	2.55736(3)
Ca1/Sr1-O8	2.51465(3)	Ca2-O9	2.36688(4)	Ca3/Sr3-O10	2.60066(5)
Ca1/Sr1-O10	2.34488(4)	Ca2-O9	2.60915(4)	Ca3/Sr3-O10	2.77217(5)
Average length	2.614	Average length	2.484	Average length	2.651
***x* = 8.0**					
Ca1/Sr1-O2	2.41026(6)	Ca2/Sr2-O2	3.14381(6)	Ca3/Sr3-O1	2.77653(7)
Ca1/Sr1-O4	2.85892(7)	Ca2/Sr2-O3	2.34875(5)	Ca3/Sr3-O2	2.65027(5)
Ca1/Sr1-O5	3.11160(7)	Ca2/Sr2-O4	2.84366(5)	Ca3/Sr3-O3	2.86901(7)

Ca1/Sr1-O6	2.60946(6)	Ca2/Sr2-O5	2.93476(5)	Ca3/Sr3-O4	2.45459(4)
Ca1/Sr1-O6	2.77057(6)	Ca2/Sr2-O7	2.39314(6)	Ca3/Sr3-O5	2.85023(5)
Ca1/Sr1-O7	2.72628(5)	Ca2/Sr2-O8	2.86655(7)	Ca3/Sr3-O7	2.67843(5)
Ca1/Sr1-O8	2.69570(5)	Ca2/Sr2-O9	2.30378(5)	Ca3/Sr3-O8	3.03607(5)
Ca1/Sr1-O9	1.97863(4)			Ca3/Sr3-O10	2.65129(6)
Ca1/Sr1-O10	2.15595(5)			Ca3/Sr3-O10	2.89363(7)
Average length (Å)	2.591	Average length (Å)	2.691	Average length (Å)	2.762
***x* = 9.0**					
Sr1-O2	2.62759(5)	Sr2-O2	2.43449(3)	Sr3-O2	2.54953(3)
Sr1-O2	3.23563(6)	Sr2-O3	2.06563(3)	Sr3-O3	3.05165(4)
Sr1-O4	3.05907(5)	Sr2-O4	2.47511(2)	Sr3-O4	2.69437(3)
Sr1-O5	2.53590(4)	Sr2-O5	2.48109(2)	Sr3-O5	2.44818(2)
Sr1-O6	2.07407(4)	Sr2-O7	2.57858(4)	Sr3-O7	2.57002(3)
Sr1-O6	2.77840(5)	Sr2-O8	2.85118(5)	Sr3-O8	2.63310(3)
Sr1-O7	2.51151(2)	Sr2-O9	2.47156(4)	Sr3-O10	2.74709(5)
Sr1-O8	2.64713(3)	Sr2-O9	2.53244(4)	Sr3-O10	2.75368(5)
Sr1-O10	2.46155(3)				
Average length (Å)	2.659	Average length (Å)	2.486	Average length (Å)	2.681

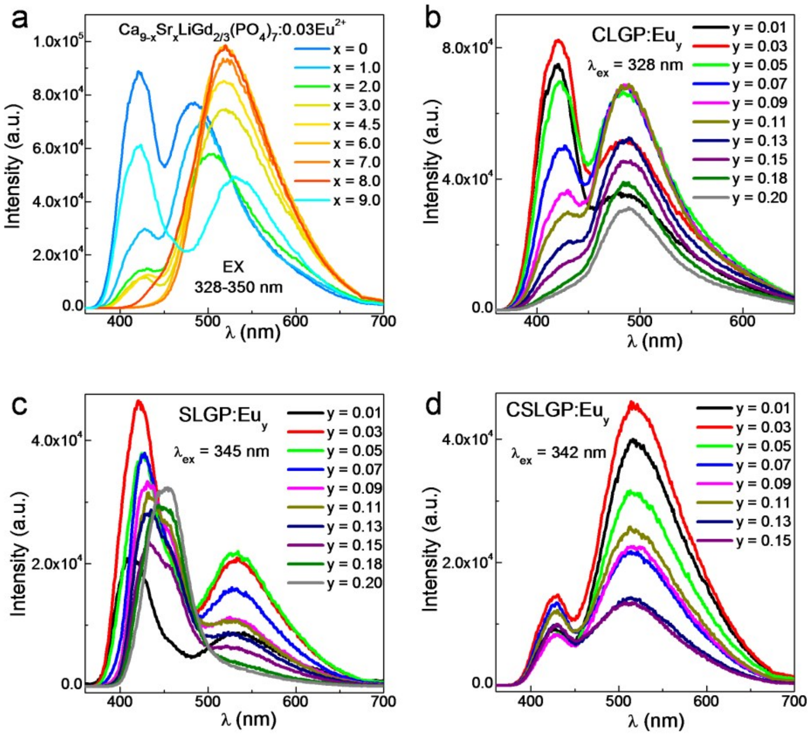

Figure S2. Emission spectra of (a) CSLGP:0.03Eu^{2+} (x = 0-9.0) samples excited under 328-350 nm wavelength (b) CLGP:$y$$Eu^{2+}$ (y = 0.01-0.20) samples excited under 328 nm wavelength (c) SLGP:$y$$Eu^{2+}$ (y = 0.01-0.20) samples excited under 345 nm wavelength and (d) CSLGP:$y$$Eu^{2+}$ (y = 0.01-0.15) samples excited under 342 nm wavelength.

Table S4. The emission wavelengths, fwhms, IQE and EQE of $Ca_{8.97-x}Sr_xLiGd_{2/3}(PO_4)_7$:$0.03Eu^{2+}$ (x = 0-9.0) samples monitored at different excitation wavelengths.

Sample	EM1 /nm	fwhm /nm	EM2 /nm	fwhm /nm	EM/nm	fwhm /nm	IQE (%)	EQE (%)
λ_{ex} = 328-350 nm								
x = 0	551.72	110.94	482.36	72.03	417.81	36.20	46.2	13.1
x = 1.0	559.76	114.25	491.63	73.05	418.68	35.41	35.6	13.1
x = 2.0	565.14	110.35	499.51	71.76	419.87	34.25	38.3	14.7
x = 3.0	568.85	104.39	511.39	70.02	421.13	33.20	42.3	14.8
x = 4.5	564.95	105.73	510.29	71.09	424.01	33.80	49.2	21.5
x = 6.0	570.85	96.88	513.39	62.70			47.7	22.1
x = 7.0	572.24	96.21	515.44	61.65			51.9	22.3
x = 8.0	572.73	99.62	513.42	76.52			52.2	23.3
x = 9.0	558.76	114.17	518.07	97.89	421.91	40.85	35.0	14.2

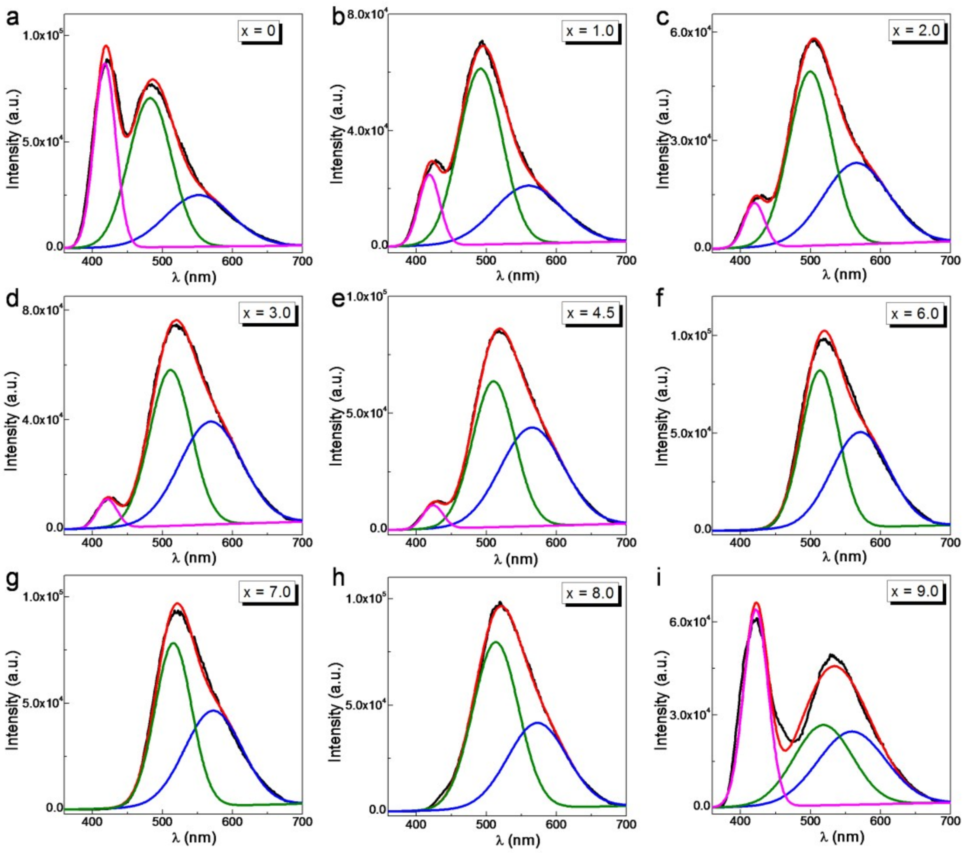

Figure S3. (a)-(i) Corresponding the Gaussian fitting peak of CSLGP:0.03Eu^{2+} samples from x = 0 to x = 9.0, respectively.

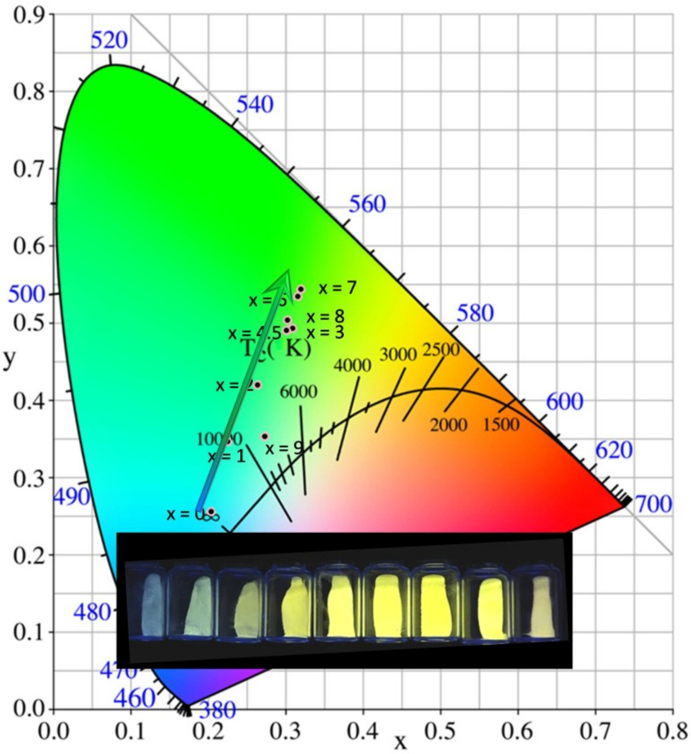

Figure S4. The corresponding CIE chromaticity coordinates diagrams and the luminescence photographs of $Ca_{8.97\text{-}x}Sr_xLiGd_{2/3}(PO_4)_7$:$0.03Eu^{2+}$ (x = 0-9.0) samples excited under different UV wavelengths (328-350 nm).

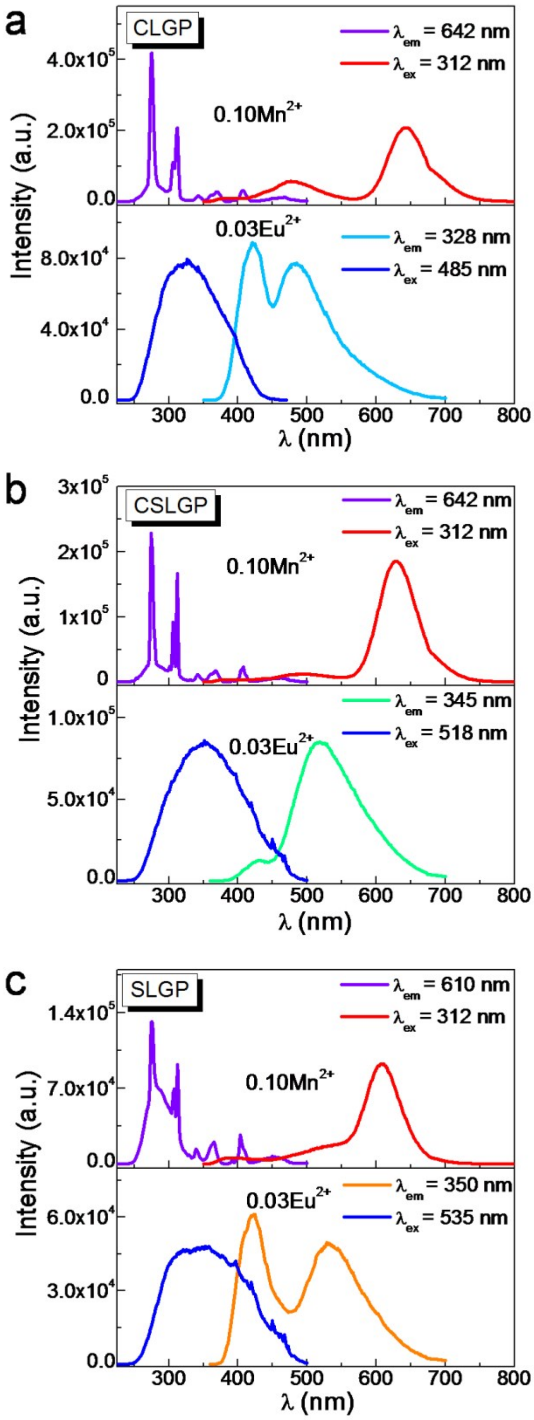

Figure S5. The PL and PLE spectra of $0.10Mn^{2+}$ and $0.03Eu^{2+}$ in single doped (a) CLGP (x = 0) (b) CSLGP (x = 4.5) and (c) SLGP (x = 9.0) component matrix, respectively.

Table S5. Main refinement parameters of the $Sr_{8.95-z}LiGd_{2/3}(PO_4)_7$:0.05$Eu^{2+}$,$z$$Mn^{2+}$ (z = 0-0.40) samples.

Space group: R3c (161), Z = 6			
x = 9.0 y = 0.05	Cell parameters, Å	Cell volume, Å^3	R_{wp}, R_p, %, χ^2
z = 0	a = b = 10.7052 c = 39.6157 α = β = 90º γ= 120°	3931.74	5.75, 3.92, 7.491
z = 0.05	a = b = 10.6943 c = 39.5862 α = β = 90º γ= 120°	3920.82	7.00, 5.00, 5.298
z = 0.10	a = b = 10.6891 c = 39.5663 α = β = 90º γ= 120°	3915.05	5.20, 3.94, 2.438
z = 0.15	a = b = 10.6807 c = 39.5466 α = β = 90º γ= 120°	3903.04	8.34, 5.61, 7.263
z = 0.20	a = b = 10.6687 c = 39.5520 α = β = 90º γ= 120°	3898.74	6.11, 4.40, 2.552
z = 0.30	a = b = 10.6661 c = 39.4490 α = β = 90º γ= 120°	3886.66	7.24, 5.05, 5.516
z =0.40	a = b = 10.6616 c = 39.3898 α = β = 90º γ= 120°	3877.56	7.21, 4.99, 5.585

Table S6. The emission wavelengths, fwhms of $Sr_{8.95-z}LiGd_{2/3}(PO_4)_7$:0.05$Eu^{2+}$,$z$$Mn^{2+}$ (z = 0-0.40) samples monitored at 350 nm at different luminescence sites.

z	EM1 (nm)	fwhm (nm)	EM2 (nm)	fwhm (nm)	EM3 (nm)	fwhm (nm)	EM4 (nm)	fwhm (nm)
0	418.89	35.49	449.05	35.88	522.41	117.53	570.82	103.26
0.05	425.79	28.10	452.05	42.63	517.45	83.20	603.82	71.85
0.10	425.55	27.69	452.41	42.58	518.24	78.53	607.30	67.22
0.15	440.77	32.20	464.30	39.51	517.70	69.11	608.08	66.19
0.20	440.04	29.55	463.80	39.99	515.49	67.29	608.83	65.59
0.25	441.83	33.94	468.70	43.53	518.19	58.60	609.42	65.03
0.30	447.39	35.38	479.78	43.19	522.13	51.28	610.44	65.80
0.40	459.52	44.84	495.13	41.52	529.32	40.52	611.65	64.98

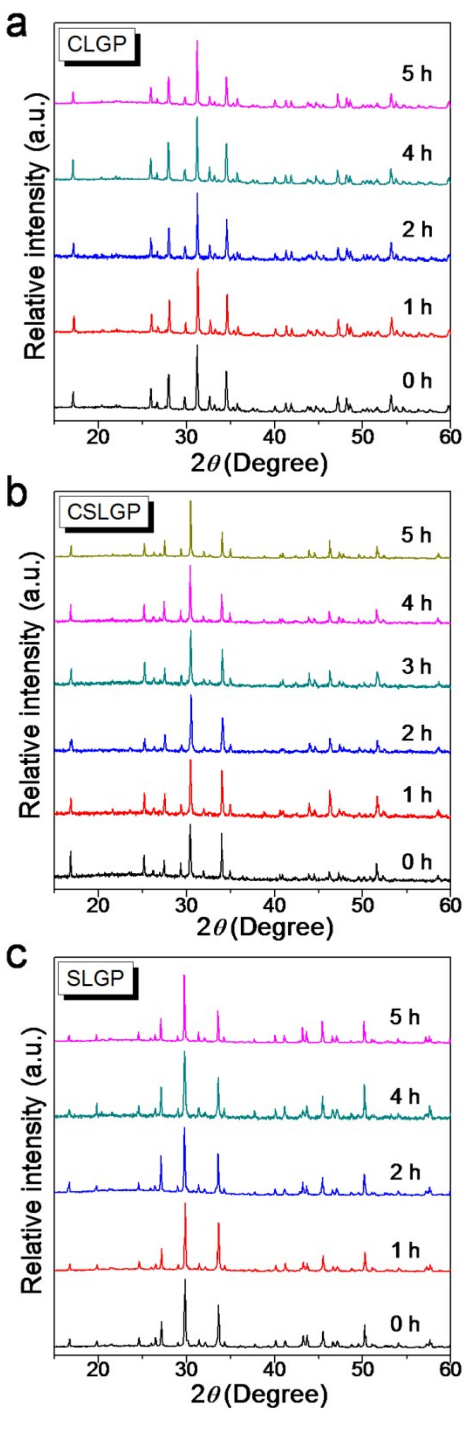

Figure S6. The XRD patterns of Eu^{2+}/Eu^{3+} doped (a) CLGP (x = 0) (b) CSLGP (x = 4.5) and (c) SLGP (x = 9.0) component matrix sintered at different time, respectively.