

Supplementary data

**Effect of Ca²⁺-ion co-doping on radiative properties via tuning the
local symmetry around the Eu³⁺ ions in orange red light emitting**

GdPO₄:Eu³⁺ phosphors

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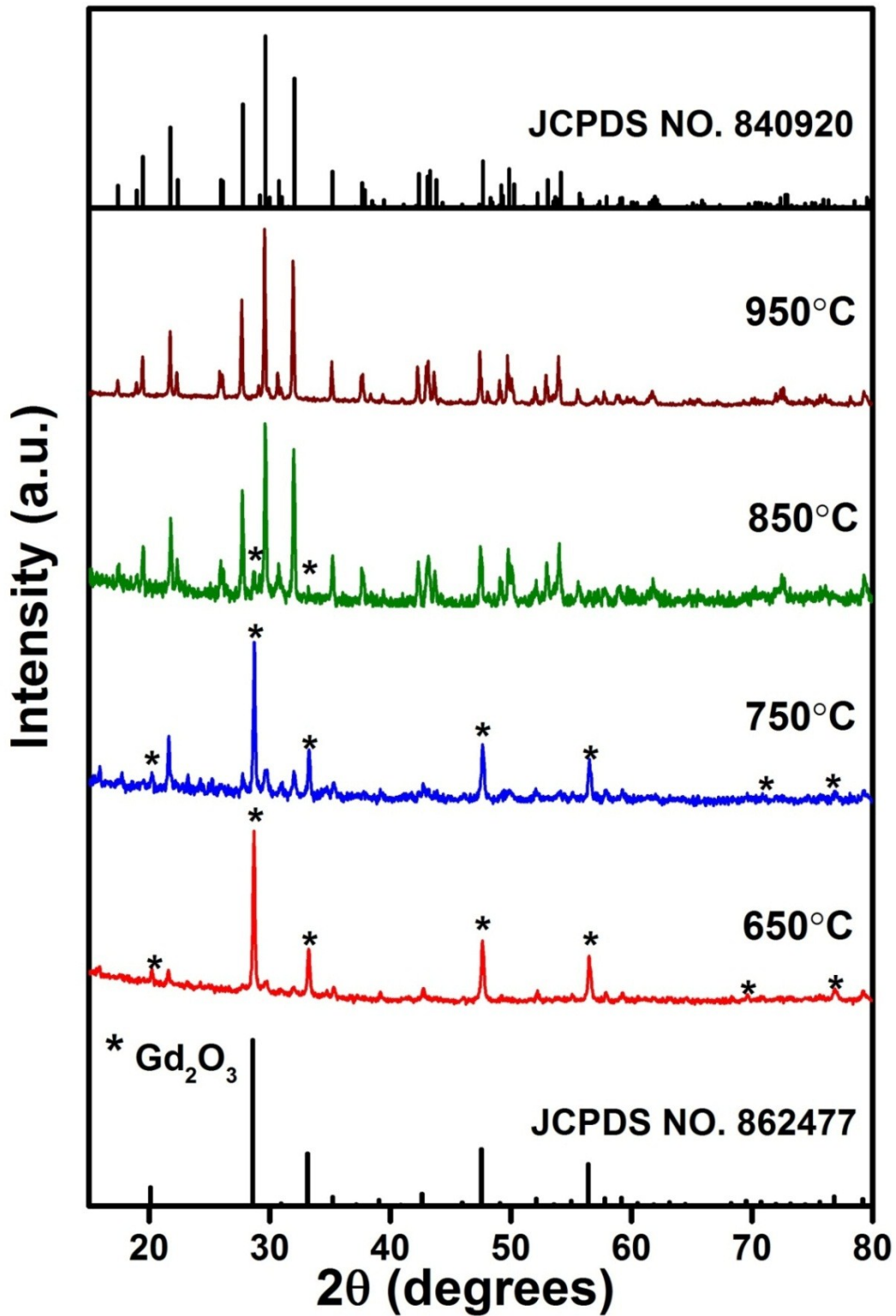


Fig. S1. Powder X-ray diffraction patterns of $\text{Gd}_{0.93}\text{Eu}_{0.07}\text{PO}_4$ phosphor calcined at different temperatures for 12 h.

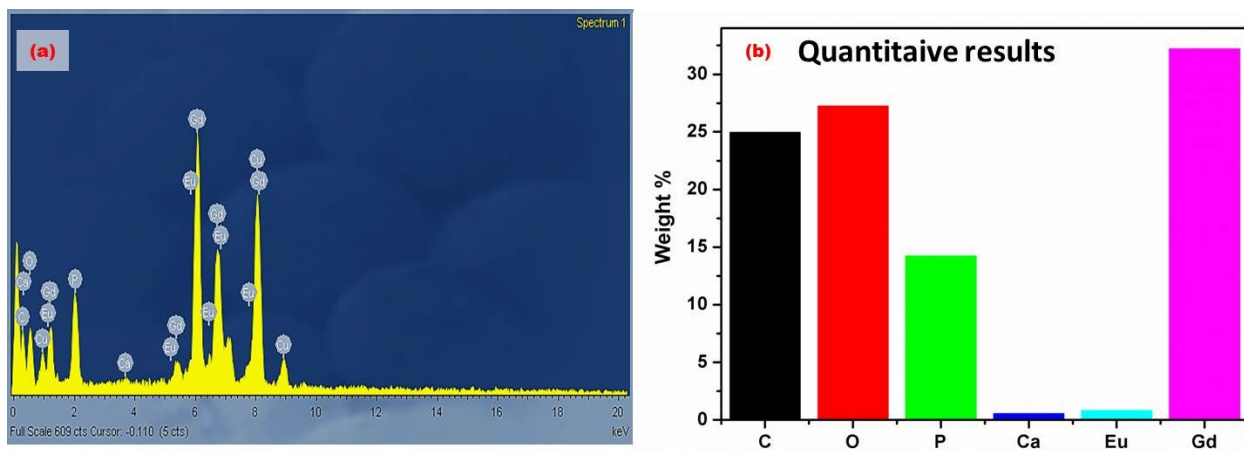


Fig. S2. EDX Spectra of $\text{Gd}_{0.86}\text{Eu}_{0.07}\text{Ca}_{0.07}\text{PO}_4$ phosphors.

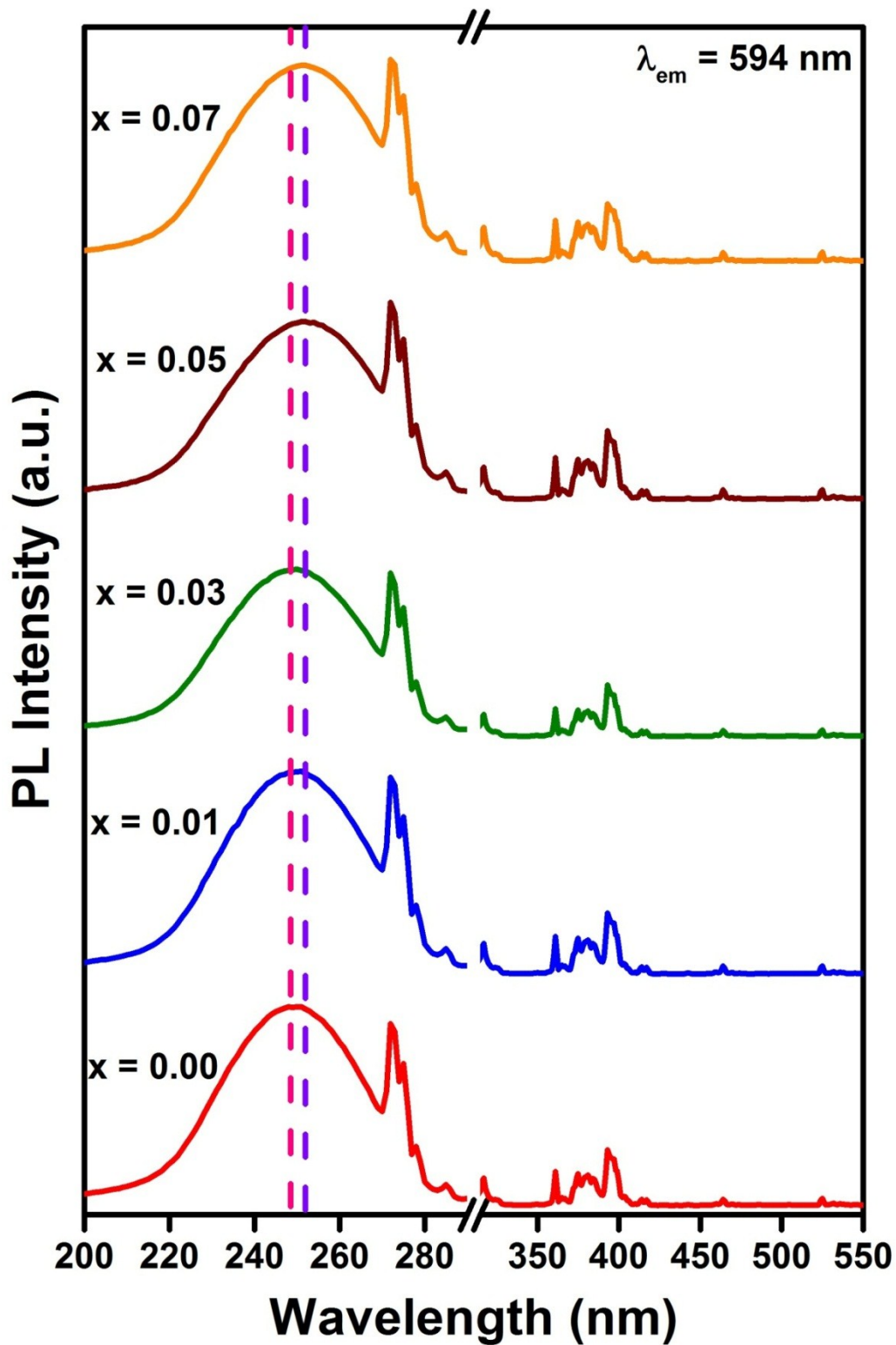


Fig.S3. Photoluminescence excitation spectra of $\text{Gd}_{0.93-x}\text{Eu}_{0.07}\text{Ca}_x\text{PO}_4$ phosphors prepared at 950 °C 12 h.

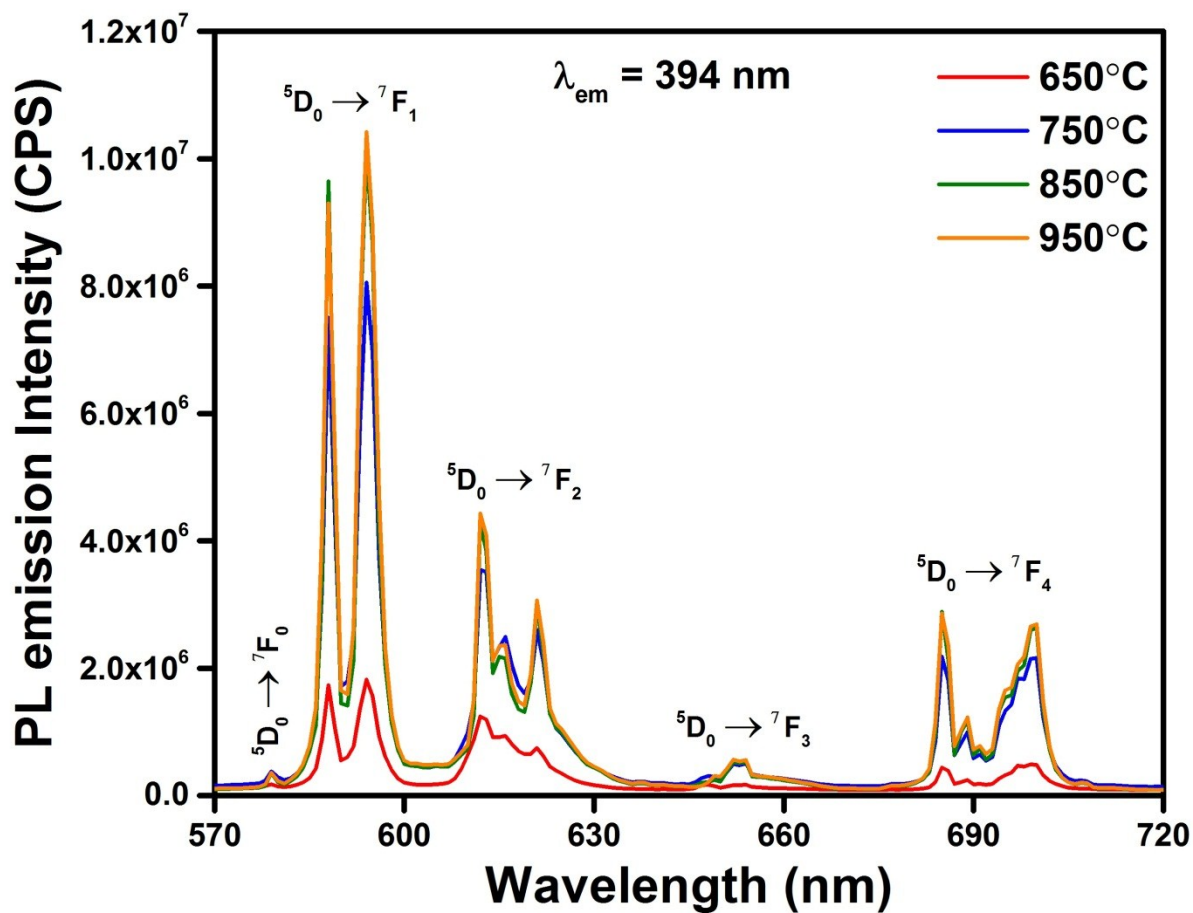


Fig. S4. Photoluminescence emission spectra for $\text{Gd}_{0.93}\text{Eu}_{0.07}\text{PO}_4$ ($\lambda_{ex} = 394 \text{ nm}$) phosphors prepared at different temperature.

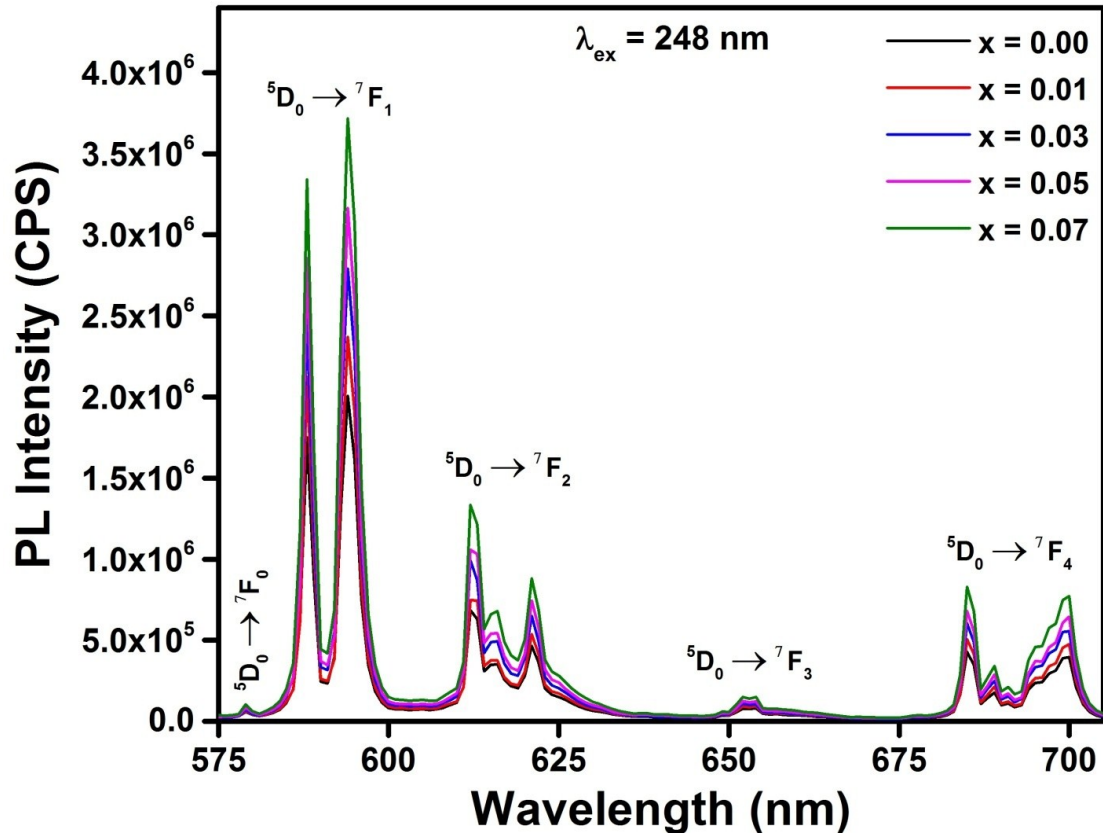


Fig. S5. Photoluminescence emission spectra of the $Gd_{0.93-x}Eu_{0.07}Ca_xPO_4$ phosphors recorded at $\lambda_{ex} = 248$ nm.

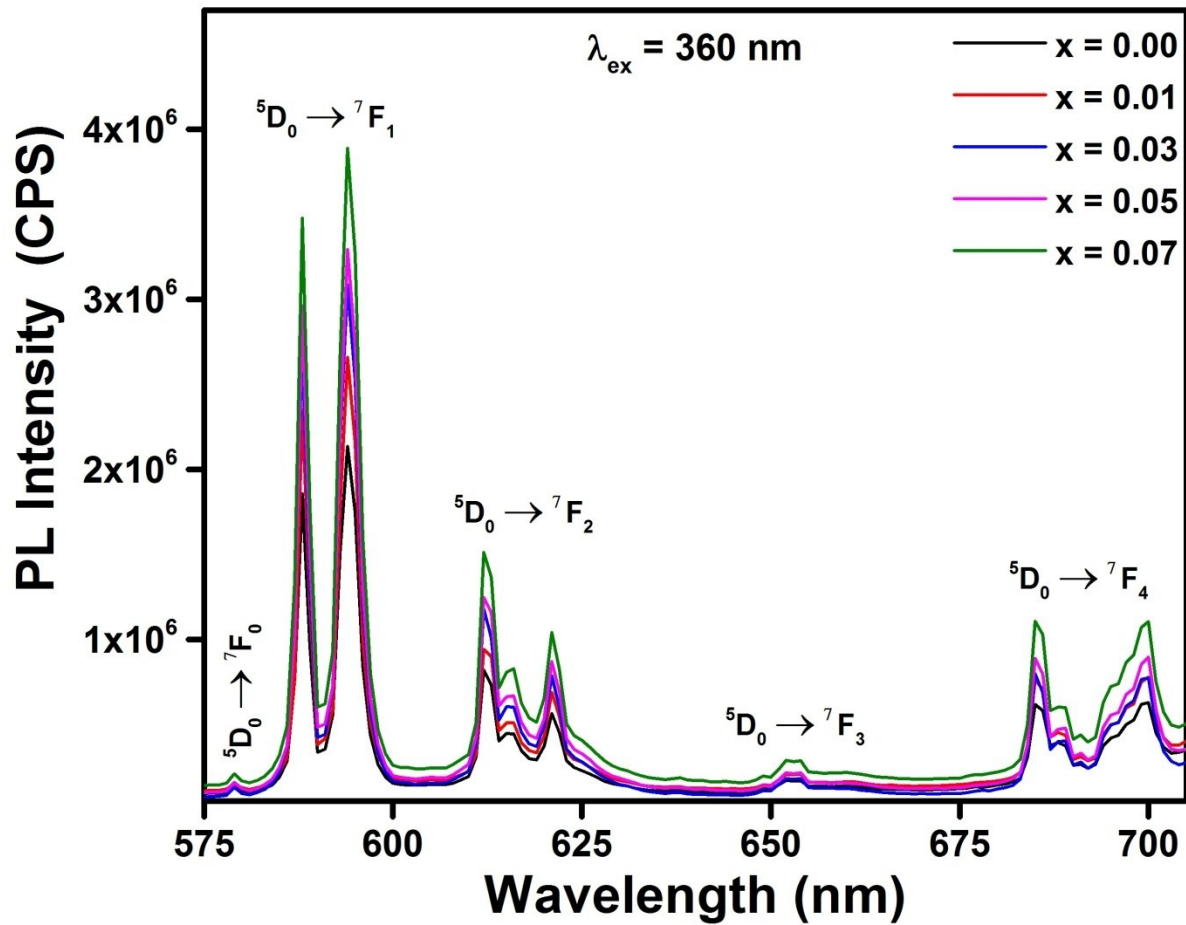


Fig. S6. Photoluminescence emission spectra of the $\text{Gd}_{0.93-x}\text{Eu}_{0.07}\text{Ca}_x\text{PO}_4$ phosphors recorded at $\lambda_{\text{ex}} = 360 \text{ nm}$.

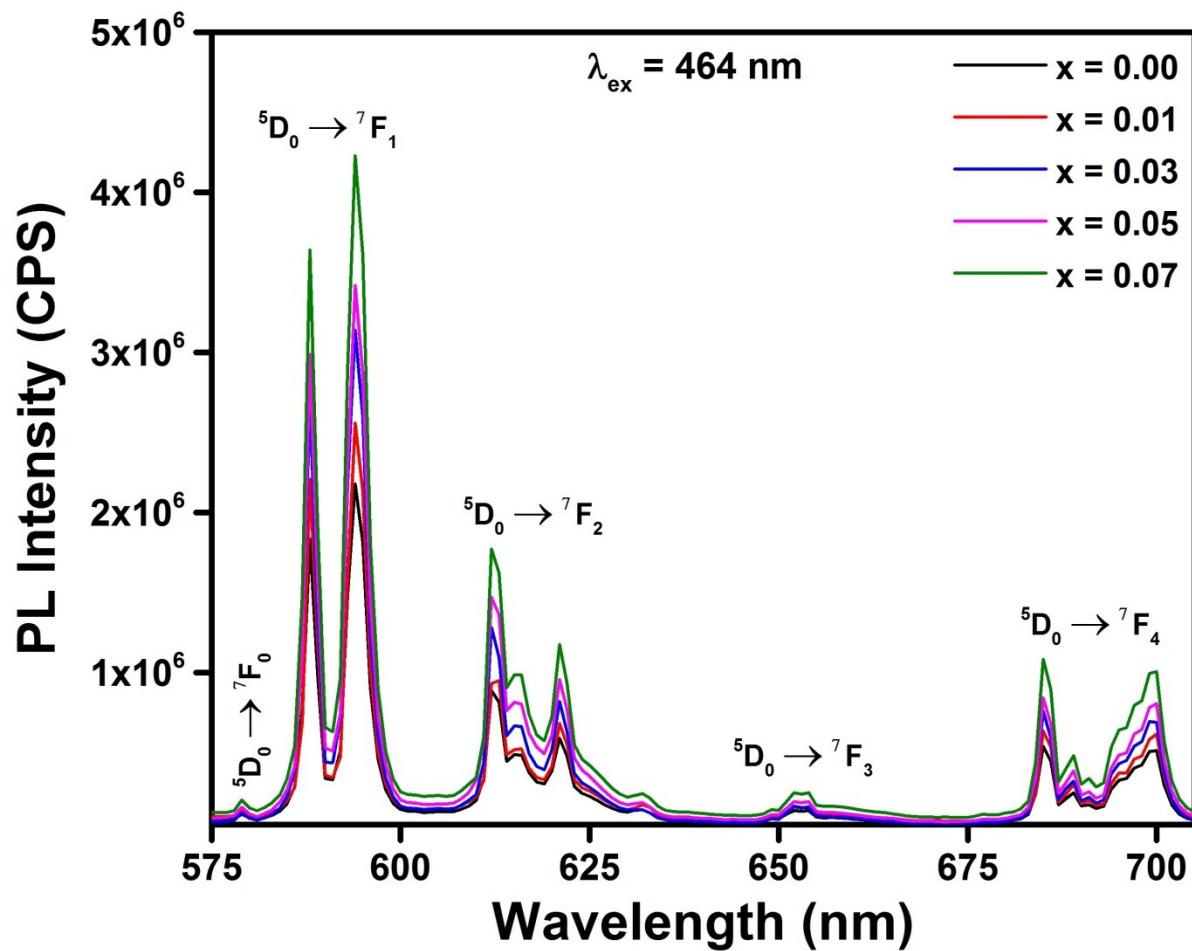


Fig. S7. Photoluminescence emission spectra of $\text{Gd}_{0.93-x}\text{Eu}_{0.07}\text{Ca}_x\text{PO}_4$ phosphors recorded at $\lambda_{\text{ex}} = 464 \text{ nm}$.

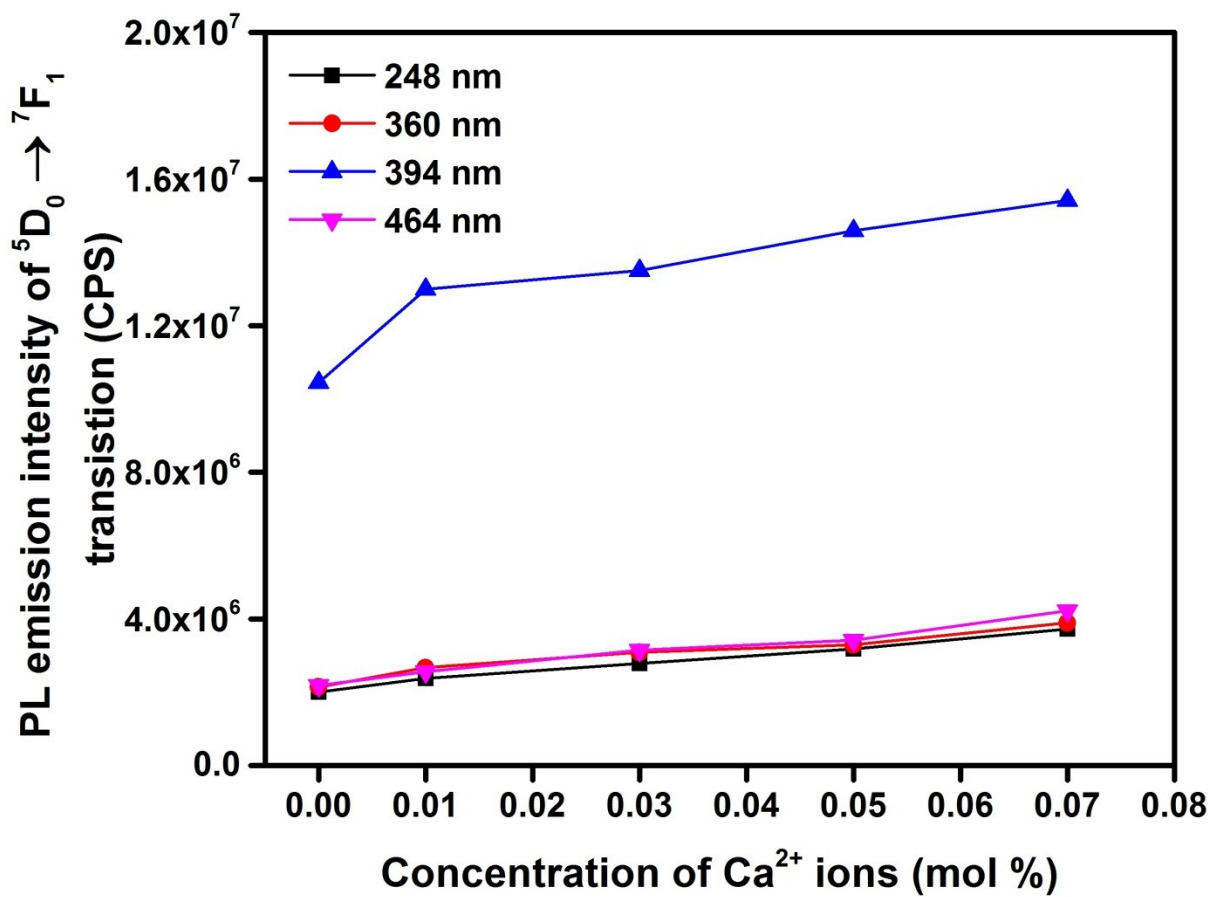


Fig. S8. Variation of emission intensity of ${}^5D_0 \rightarrow {}^7F_1$ peaks as a function of Ca^{2+} ions concentration at different excitation wavelengths.

Table S1. Rietveld refined structural parameters for $\text{Gd}_{0.93-x}\text{Eu}_{0.07}\text{Ca}_x\text{PO}_4$ ($0.00 \leq x \leq 0.07$) phosphors.

Ca ²⁺ content	Ca ²⁺ (0 mol%)	Ca ²⁺ (1 mol%)	Ca ²⁺ (3 mol%)	Ca ²⁺ (5 mol%)	Ca ²⁺ (7 mol%)
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P12 _{1/n} 1 (14)	P 12 _{1/n} 1 (14)	P12 _{1/n} 1 (14)	P12 _{1/n} 1 (14)	P12 _{1/n} 1 (14)
Lattice Parameters					
<i>a</i> (Å)	6.653(2)	6.654(3)	6.654(3)	6.655(3)	6.655(2)
<i>b</i> (Å)	6.850(1)	6.847(2)	6.848(4)	6.848(2)	6.849(3)
<i>c</i> (Å)	6.339(2)	6.339(1)	6.340(3)	6.341(2)	6.341(2)
Cell volume (Å ³)	280.02(7)	280.21(2)	280.33(1)	280.38(2)	280.43(7)
β (°)	103.99(7)	104.00(2)	104.01(5)	104.02(1)	104.02(2)
Atomic positions					
Gd ³⁺ /Eu ³⁺ /Ca ²⁺	(4b)	(4b)	(4b)	(4b)	(4b)
<i>x</i>	0.2812(24)	0.2801(34)	0.2809(44)	0.2818(34)	0.2813(35)
<i>y</i>	0.1554(29)	0.1547(42)	0.1549(53)	0.1552(42)	0.1552(42)
<i>z</i>	0.0963(31)	0.0961(44)	0.0948(58)	0.0952(45)	0.0957(45)
P	(4a)	(4a)	(4a)	(4a)	(4a)
<i>x</i>	0.3030 (10)	0.3004(9)	0.3005(18)	0.2987(14)	0.2997(23)
<i>y</i>	0.1602 (11)	0.1614(15)	0.1598(19)	0.1610(13)	0.1607(21)
<i>z</i>	0.6179 (9)	0.6181(14)	0.6213(17)	0.6169(11)	0.6153(22)
O1	(16f)	(16f)	(16f)	(16f)	(16f)
<i>x</i>	0.2425(19)	0.2429(27)	0.2350(24)	0.2477(25)	0.2465(40)
<i>y</i>	-0.0013(18)	-0.0010(18)	-0.0077(24)	-0.0015(22)	-0.0067(36)
<i>z</i>	0.4291(23)	0.4275(32)	0.4203(43)	0.4177(24)	0.4301(43)
O2	(16f)	(16f)	(16f)	(16f)	(16f)
<i>x</i>	0.3822(13)	0.3812(18)	0.3783(23)	0.3858(18)	0.3872(27)
<i>y</i>	0.3303(20)	0.3261(27)	0.3187(32)	0.3357(28)	0.3297(39)
<i>z</i>	0.5026(19)	0.5038(26)	0.5019(33)	0.5081(25)	0.5023(41)
O3	(16f)	(16f)	(16f)	(16f)	(16f)
<i>x</i>	0.4757(16)	0.4688(22)	0.4673(29)	0.4730(22)	0.4739(27)
<i>y</i>	0.1045(15)	0.1071(21)	0.1055(33)	0.1009(19)	0.1019(20)

z	0.8113(16)	0.8096(22)	0.8070(31)	0.8133(23)	0.8160(23)
O4	(16f)	(16f)	(16f)	(16f)	(16f)
x	0.1208(17)	0.1175(24)	0.1138(30)	0.1138(23)	0.1033(23)
y	0.1996(18)	0.2023(25)	0.1952(33)	0.1974(25)	0.1997(25)
z	0.7144(18)	0.7176(26)	0.7049(31)	0.7080(24)	0.7073(24)
R Factors					
R_p	1.33	1.65	1.95	1.63	1.64
R_{wp}	1.75	2.09	2.45	2.07	2.08
R_{exp}	1.58	2.20	2.53	2.25	2.25
χ^2	1.23	0.90	0.94	0.84	0.85
R_{Bragg}	5.49	6.31	8.53	5.90	6.41
R_F	5.33	5.73	6.63	5.51	6.29
