

Photoluminescent tuning of $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{Ce}^{3+}/\text{Eu}^{2+}$, $\text{Tb}^{3+}/\text{Mn}^{2+}$ phosphors: Structure refinement, site occupancy, energy transfer and thermal stability

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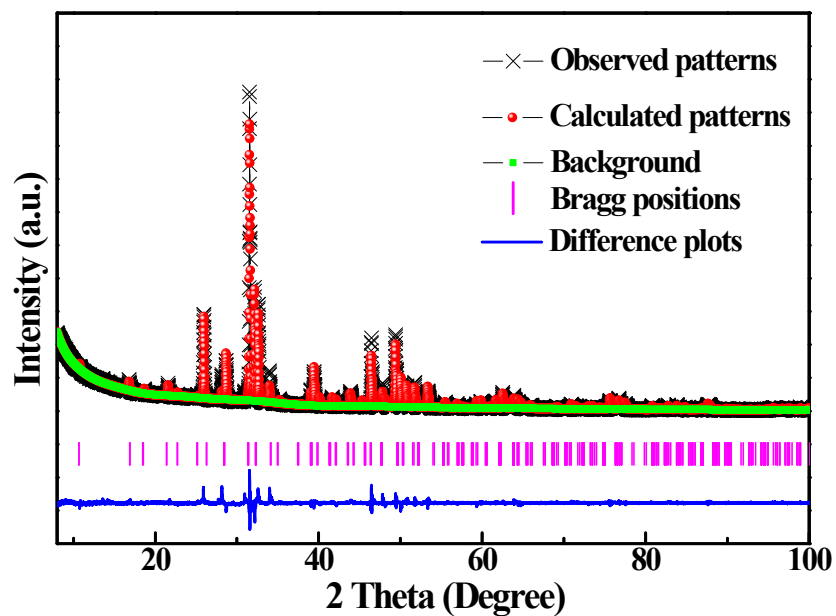


Figure S1. (a) Experimental (black crosses) and calculated (red solid line) XRD patterns and their difference (blue solid line) for the Rietveld fit of CPOCl:0.10Ce³⁺ XRD pattern by the GSAS program. The short vertical lines show the positions of Bragg reflections of the calculated pattern.

Table S1 Structure parameters of CPOCl:0.10Ce^{3+} derived from the GSAS refinement of XRD data.

Atom	Wyckoff position	X	Y	Z
Ca1/Eu 1	$4f$	0.3333000(0)	0.6667000(0)	0.0001000(0)
Ca2/Eu 2	$6h$	0.2350800(0)	-	0.2500000(0)
P	$6h$	0.4036710(0)	0.3731130(0)	0.2500000(0)
O1	$6h$	0.3344100(0)	0.4842290(0)	0.2500000(0)
O2	$6h$	0.5985850(0)	0.4715580(0)	0.2500000(0)
O3	$12i$	0.3504860(0)	0.2696650(0)	0.0743480(0)
Cl	$2b$	0.0000000(0)	0.0000000(0)	0.0000000(0)

Cell parameters: $a = b = 9.509 \text{ \AA}$, $c = 6.865 \text{ \AA}$;
 $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$;

$V = 537.60 \text{ \AA}^3$ and $Z = 2$;

Space group: $P63/m$ (176);

Reliability factor: $R_{\text{wp}} = 8.90\%$, $R_{\text{p}} = 5.16\%$ and $\chi^2 = 7.047$

Table S2 Selected interatomic distances in CPOCl:0.10Ce³⁺.

Bond	Length (Å)	Bond	Length (Å)
Ca1/Ce1- O1	2.4439(29)	Ca2/Ce2- O1	2.76999 (3)
Ca1/Ce1- O1	2.4435(29)	Ca2/Ce2- O2	2.41764 (3)
Ca1/Ce1- O1	2.4432(29)	Ca2/Ce2- O3	2.61004 (3)
Ca1/Ce1- O2	2.4382(29)	Ca2/Ce2- O3	2.39620 (3)
Ca1/Ce1- O2	2.4388(29)	Ca2/Ce2- O3	2.39620 (3)
Ca1/Ce1- O2	2.4383(29)	Ca2/Ce2- O3	2.61004 (2)
Ca1/Ce1- O3	2.8017(7)	Ca2/Ce2-C 11	2.85736 (3)
Ca1/Ce1- O3	3.8008(7)	Ca2/Ce2-C 11	2.85736 (3)
Ca1/Ce1- O3	2.8014(7)	—	—
Average Ca1/Ce1- O	2.67	Average Ca2/Ce2- O/Cl	2.61

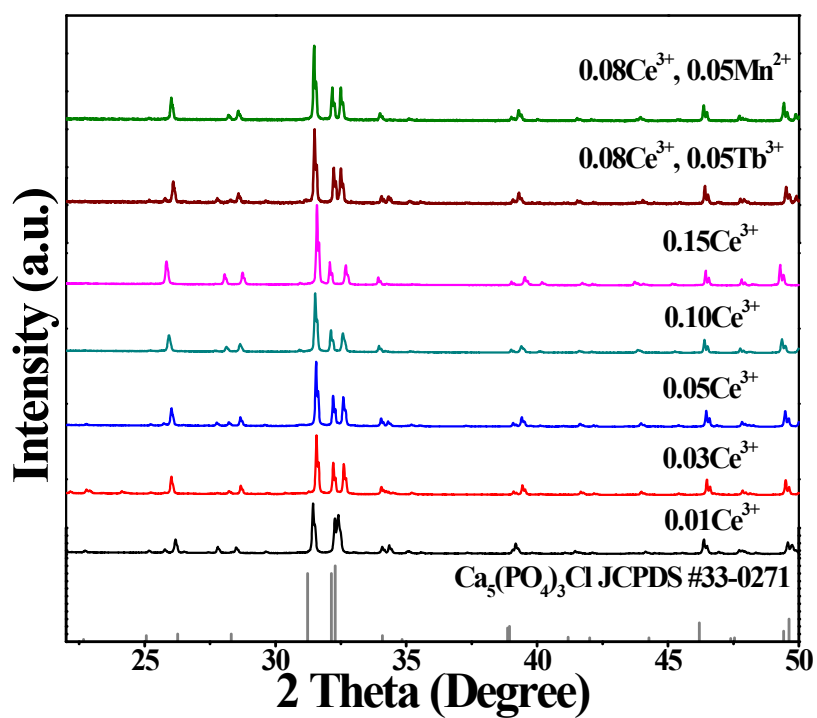


Figure S2. The XRD patterns of $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:m\text{Ce}^{3+}$ ($m = 0.01, 0.03, 0.05, 0.10, 0.15$), $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:0.08\text{Ce}^{3+}, 0.05\text{Tb}^{3+}$, and $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:0.08\text{Ce}^{3+}, 0.05\text{Mn}^{2+}$ samples. The standard $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ data (JCPDS #33-0271) is shown as a reference.

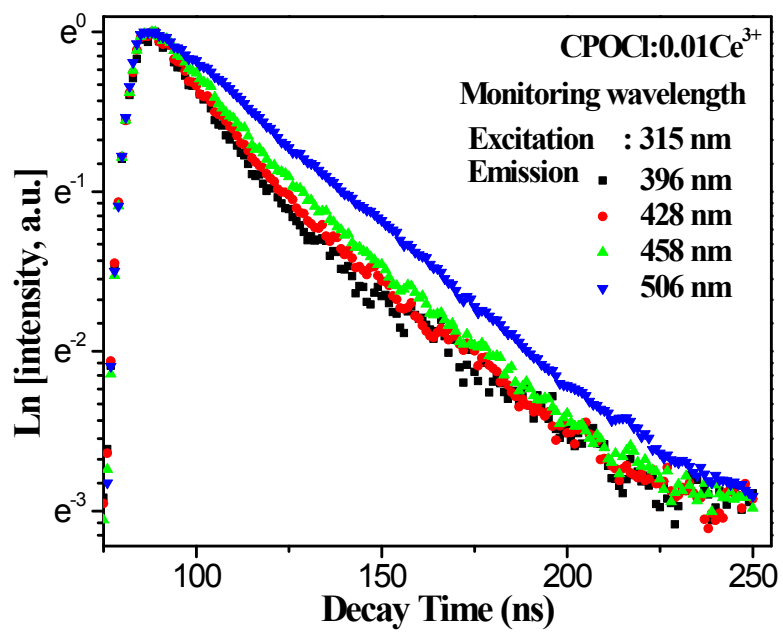


Figure S3. Decay curves of Ce³⁺ emission monitored at 320 nm (Excitation) and different emissions (396, 428, 458, 506 nm) for CPOCl:0.01Ce³⁺.

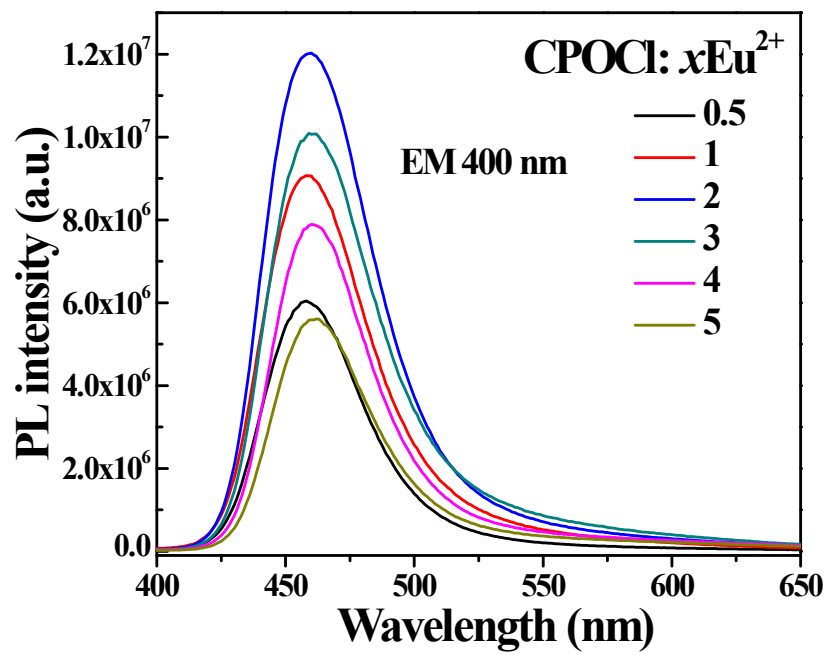


Figure S4. The PL spectra of CPOCl: $x\text{Eu}^{2+}$ ($x = 0.5-5$ mol%) samples.

Table S3 Selected interatomic distances in CPOCl:0.08Ce³⁺ and
CPOCl:0.08Ce³⁺, 0.05Mn²⁺ samples

Bond	Length (Å)	Bond	Length (Å)
CPOCl:0.08Ce ³⁺			
Ca1_O1	2.43948(2)	Ca2_O1	2.79670(3)
Ca1_O1	2.43913(2)	Ca2_O2	2.38548(3)
Ca1_O1	2.43880(2)	Ca2_O3	2.56460(2)
Ca1_O2	2.43888(2)	Ca2_O3	2.35468(3)
Ca1_O2	2.43952(2)	Ca2_O3	2.35468(3)
Ca1_O2	2.43899(2)	Ca2_O3	2.56460(2)
Ca1_O3	2.81628(3)	Ca2_Cl1	2.90104(3)
Ca1_O3	2.81536(3)	Ca2_Cl1	2.90104(3)
Ca1_O3	2.81599(3)	_____	_____
Average Ca1-O	2.56	Average Ca2-O/Cl	2.62
CPOCl:0.08Ce ³⁺ , 0.05Mn ²⁺			
Ca1_O1	2.37860(2)	Ca2_O1	2.84134(3)
Ca1_O1	2.37824(2)	Ca2_O2	2.41043(2)
Ca1_O1	2.37791(2)	Ca2_O3	2.58481(2)
Ca1_O2	2.46873(2)	Ca2_O3	2.35194(2)
Ca1_O2	2.46936(2)	Ca2_O3	2.35194(2)
Ca1_O2	2.46883(2)	Ca2_O3	2.58481(2)
Ca1_O3	2.83179(2)	Ca2_Cl1	2.91804(2)

Bond	Length (Å)	Bond	Length (Å)
Ca1_O3	2.83087(2)	Ca2_Cl1	2.91804(2)
Ca1_O3	2.83150(2)	_____	_____
Average Ca1-O	2.56	Average Ca2-O/Cl	2.60

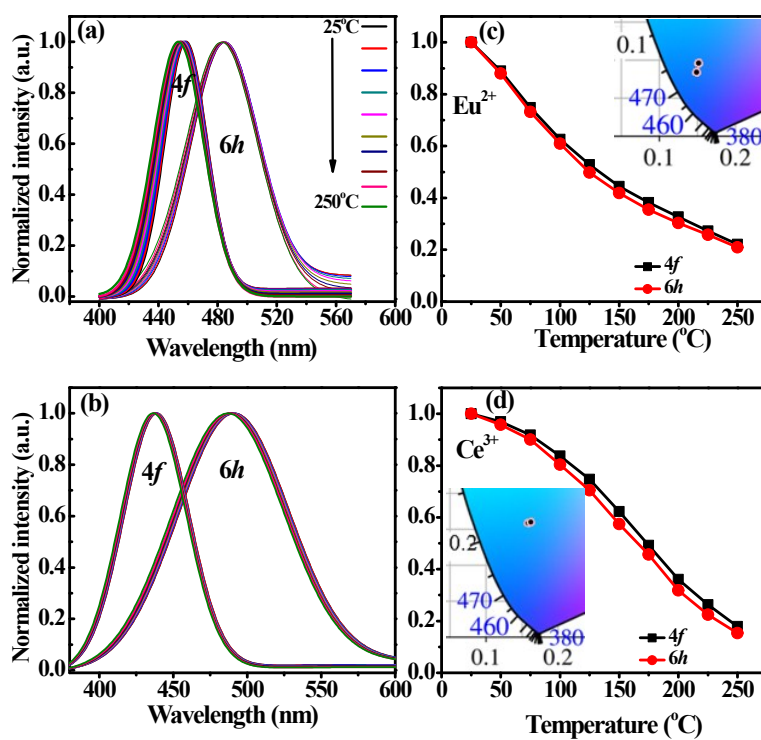


Figure S5. The Normalized Gaussian fitting PL spectra decomposed from $4f$ and $6h$ sites of (a) CPOCl:0.02Eu^{2+} and (c) CPOCl:0.10Ce^{3+} sample. The relative emission intensity of Gaussian fitting PL spectra decomposed from $4f$ and $6h$ sites of (c) CPOCl:0.02Eu^{2+} and (d) CPOCl:0.10Ce^{3+} sample with temperatures. The inserts in (c) and (d) are their CIE color coordinates at 25°C and 250°C .

