# Site-preferential Occupancy Induced Photoluminescence Tuning in $(Ca,Ba)_5(PO_4)_3Cl:Eu^{2+}$ Phosphors

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**Table S1**. Selected interatomic distances in $Ca_{4.9(1-x)}Ba_{4.9x}Eu_{0.1}(PO_4)_3Cl$ ($x$ = 0, 0.25, 0.5, 0.75, 1) samples.

| Bond | Length (Å) | Bond | Length (Å) | Bond | Length (Å) | Bond | Length (Å) |
|---|---|---|---|---|---|---|---|
| | | | x = 0 | | | | |
| Ca1_O1 | 2.59344(2) | | | Ca2_O1 | 3.10307(3) | | |
| Ca1_O1 | 2.59371(2) | | | Ca2_O2 | 2.28681(2) | | |
| Ca1_O1 | 2.59414(2) | | | Ca2_O3 | 2.44955(2) | | |
| Ca1_O2 | 2.43765(2) | | | Ca2_O3 | 2.32385(3) | | |
| Ca1_O2 | 2.43699(2) | | | Ca2_O3 | 2.44955(2) | | |
| Ca1_O2 | 2.43709(2) | | | Ca2_O3 | 2.32385(3) | | |
| Ca1_O3 | 2.84119(3) | | | Ca2_Cl1 | 3.00308(2) | | |
| Ca1_O3 | 2.84054(3) | | | Ca2_Cl1 | 3.00308(2) | | |
| Ca1_O3 | 2.84146(3) | | | | | | |
| Ca1-O | 2.624 | | | Ca2-O | 2.618 | | |
| | | | x = 0.25 | | | | |
| Ca1_O1 | 2.21693(3) | Ca2_O1 | 3.09359(6) | Ba1_O1 | 2.59365(4) | Ba2_O1 | 3.09923(6) |
| Ca1_O1 | 2.21718(3) | Ca2_O2 | 2.45664(5) | Ba1_O1 | 2.59386(4) | Ba2_O2 | 2.44036(5) |
| Ca1_O1 | 2.21771(3) | Ca2_O3 | 2.75879(4) | Ba1_O1 | 2.59432(4) | Ba2_O3 | 2.73606(4) |
| Ca1_O2 | 2.78134(4) | Ca2_O3 | 2.40705(4) | Ba1_O2 | 2.34602(3) | Ba2_O3 | 2.41245(4) |
| Ca1_O2 | 2.78078(4) | Ca2_O3 | 2.75879(4) | Ba1_O2 | 2.34536(3) | Ba2_O3 | 2.73606(4) |
| Ca1_O2 | 2.78089(4) | Ca2_O3 | 2.40705(4) | Ba1_O2 | 2.34549(3) | Ba2_O3 | 2.41245(4) |
| Ca1_O3 | 2.94914(5) | Ca2_Cl1 | 3.03689(4) | Ba1_O3 | 2.80595(5) | Ba2_Cl1 | 3.03805(4) |
| Ca1_O3 | 2.94854(5) | Ca2_Cl1 | 3.03689(4) | Ba1_O3 | 2.80532(5) | Ba2_Cl1 | 3.03805(4) |
| Ca1_O3 | 2.94944(5) | | | Ba1_O3 | 2.80627(5) | | |
| Ca1-O | 2.649 | Ca2-O | 2.744 | Ba1-O | 2.582 | Ba2-O | 2.739 |
| | | | x = 0.50 | | | | |
| Ca1_O1 | 2.04326(8) | Ca2_O1 | 3.05540(14) | Ba1_O1 | 2.62773(9) | Ba2_O1 | 3.03765(14) |
| Ca1_O1 | 2.04356(8) | Ca2_O2 | 2.64265(12) | Ba1_O1 | 2.62797(9) | Ba2_O2 | 2.63774(12) |
| Ca1_O1 | 2.04411(8) | Ca2_O3 | 2.86230(11) | Ba1_O1 | 2.62839(9) | Ba2_O3 | 2.87678(11) |
| Ca1_O2 | 3.21773(12) | Ca2_O3 | 2.46174(11) | Ba1_O2 | 2.50018(8) | Ba2_O3 | 2.45413(11) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ca1_O2 | 3.21724(12) | Ca2_O3 | 2.86230(11) | Ba1_O2 | 2.49955(8) | Ba2_O3 | 2.87678(11) |
| Ca1_O2 | 3.21726(12) | Ca2_O3 | 2.46174(11) | Ba1_O2 | 2.49957(8) | Ba2_O3 | 2.45413(11) |
| Ca1_O3 | 2.99044(11) | Ca2_Cl1 | 3.12537(11) | Ba1_O3 | 2.71837(12) | Ba2_Cl1 | 3.13710(11) |
| Ca1_O3 | 2.98985(11) | Ca2_Cl1 | 3.12537(11) | Ba1_O3 | 2.71773(12) | Ba2_Cl1 | 3.13710(11) |
| Ca1_O3 | 2.99073(11) | | | Ba1_O3 | 2.71869(12) | | |
| Ca1-O | 2.750 | Ca2-O | 2.825 | Ba1-O | 2.615 | Ba2-O | 2.826 |
| | | | x = 0.75 | | | | |
| Ca1_O2 | 2.30322(2) | Ca2_O1 | 1.24925(1) | Ba1_O1 | 2.65509(2) | Ba2_O1 | 2.93615(2) |
| Ca1_O2 | 2.30236(2) | Ca2_O1 | 2.74718(2) | Ba1_O1 | 2.65540(2) | Ba2_O2 | 2.29168(2) |
| Ca1_O2 | 2.30256(2) | Ca2_O2 | 3.06848(2) | Ba1_O1 | 2.65582(2) | Ba2_O3 | 3.02548(2) |
| Ca1_O3 | 3.16331(3) | Ca2_O3 | 2.79558(2) | Ba1_O2 | 2.83637(2) | Ba2_O3 | 2.49210(2) |
| Ca1_O3 | 3.16295(3) | Ca2_O3 | 2.67251(2) | Ba1_O2 | 2.83567(2) | Ba2_O3 | 3.02548(2) |
| Ca1_O3 | 3.16232(3) | Ca2_O3 | 2.79558(2) | Ba1_O2 | 2.83583(2) | Ba2_O3 | 2.49210(2) |
| Ca1_O1 | 3.34739(2) | Ca2_Cl1 | 4.14668(2) | Ba1_O3 | 3.10868(3) | Ba2_Cl1 | 3.19551(2) |
| Ca1_O1 | 3.34739(2) | Ca2_Cl1 | 4.14668(2) | Ba1_O3 | 3.10807(3) | Ba2_Cl1 | 3.19551(2) |
| Ca1_O1 | 3.34739(2) | | | Ba1_O3 | 3.10905(3) | | |
| Ca1-O | 2.938 | Ca2-O | 2.922 | Ba1-O | 2.900 | Ba2-O | 2.832 |
| | | | x = 1 | | | | |
| Ba1_O1 | 2.85002(1) | | | Ba2_O1 | 3.09801(2) | | |
| Ba1_O1 | 2.85031(1) | | | Ba2_O2 | 2.90283(2) | | |
| Ba1_O1 | 2.85077(1) | | | Ba2_O3 | 2.81374(1) | | |
| Ba1_O2 | 2.64436(1) | | | Ba2_O3 | 2.71775(2) | | |
| Ba1_O2 | 2.64376(1) | | | Ba2_O3 | 2.81374(1) | | |
| Ba1_O2 | 2.64373(1) | | | Ba2_O3 | 2.71775(2) | | |
| Ba1_O3 | 3.09412(2) | | | Ba2_Cl1 | 3.22378(1) | | |
| Ba1_O3 | 3.09345(2) | | | Ba2_Cl1 | 3.22378(1) | | |
| Ba1_O3 | 3.09443(2) | | | | | | |
| Ba1-O | 2.863 | | | Ba2-O | 2.939 | | |

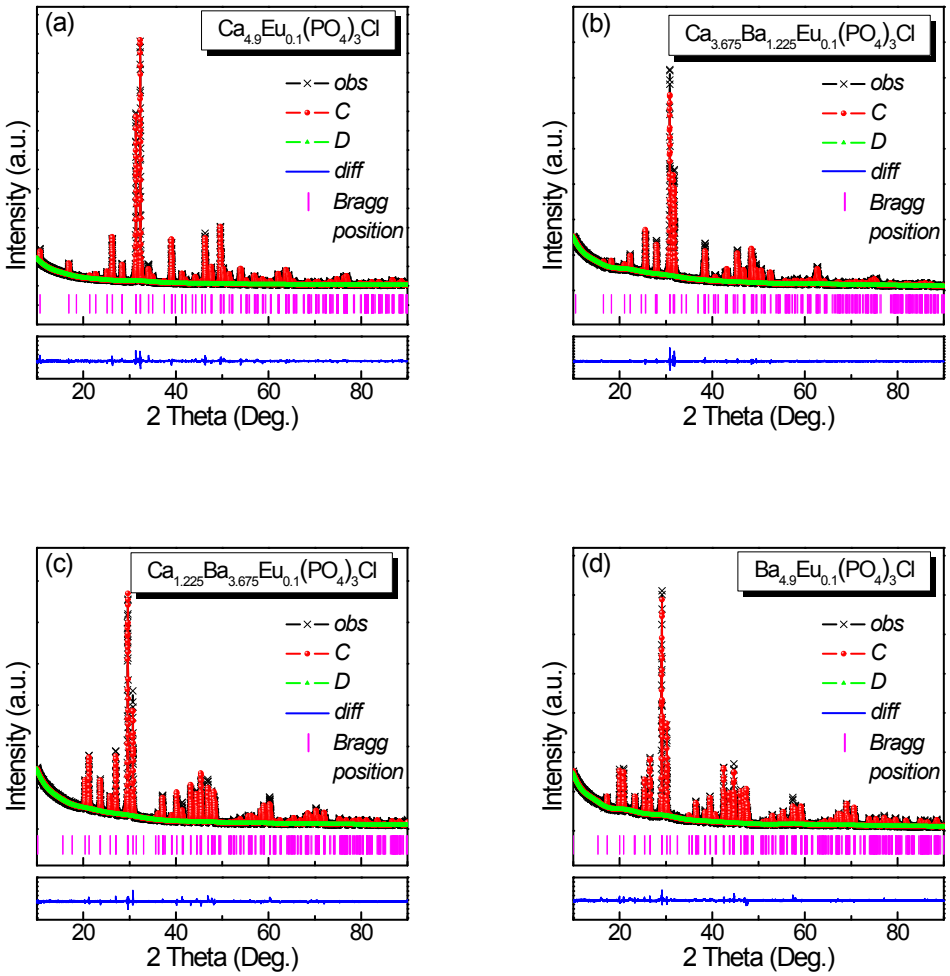


**Figure S1**. The Rietveld fit of (a) $Ca_{4.9}Eu_{0.1}(PO_4)_3Cl$, (b) $Ca_{3.675}Ba_{1.225}Eu_{0.1}(PO_4)_3Cl$, (c) $Ca_{1.225}Ba_{3.675}Eu_{0.1}(PO_4)_3Cl$ and (d) $Ba_{4.9}Eu_{0.1}(PO_4)_3Cl$ XRD patterns by the GSAS program.

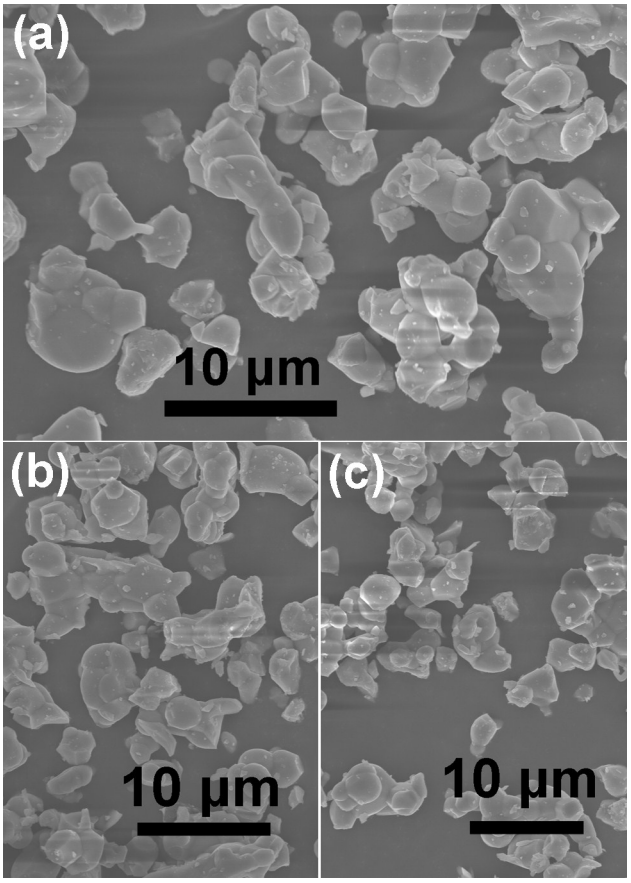


**Figure S2**. The SEM image of the representative samples: (a) CPOCl, (b) CPOCl-$Ba_{0.5}$ and (c) BPOCl.

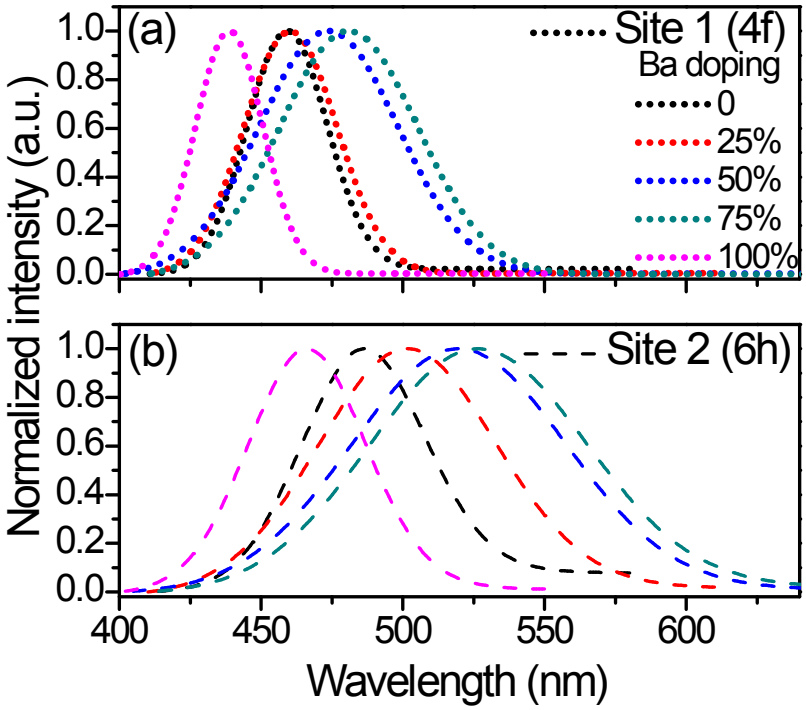


**Figure S3.** The normalized Gaussian peaks fitting photoluminescence emission (PL) spectra of $Ca_{4.9(1-x)}Ba_{4.9x}Eu_{0.1}(PO_4)_3Cl$ ($x$ = 0, 0.25, 0.5, 0.75, 1) samples at (a) 4*f* sites and (b) 6*h* sites, respectively.

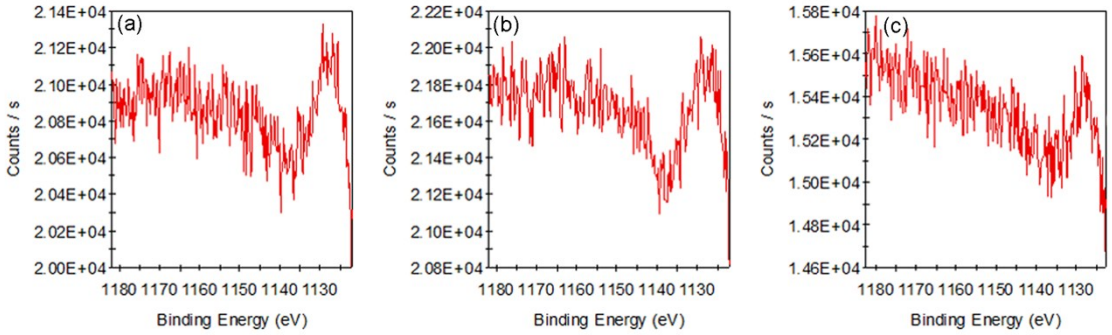


**Figure S4**. The high resolution Eu 3d XPS spectra for the representative samples: (a) CPOCl, (b) CPOCl-$Ba_{0.5}$ and (c) BPOCl.

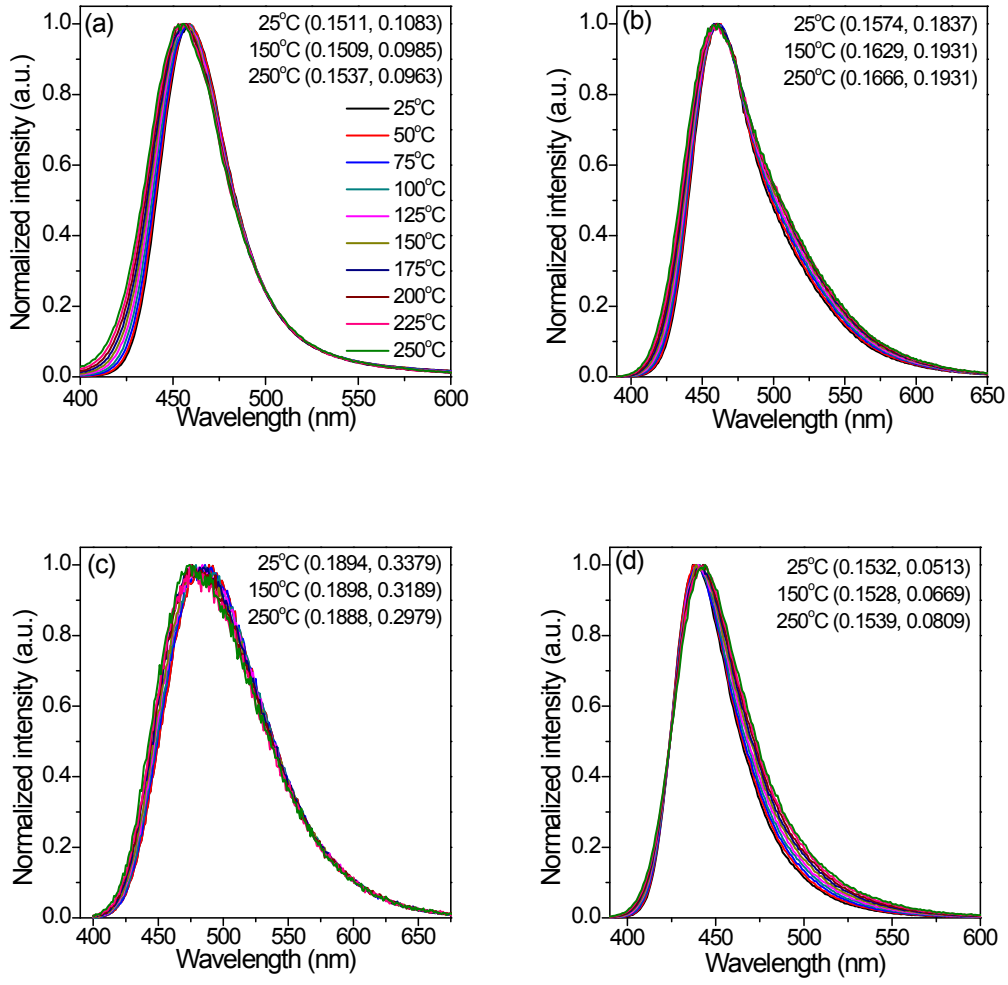


**Figure S5.** The normalized PL spectra of $Ca_{2.45}Ba_{2.45}Eu_{0.1}(PO_4)_3Cl$ (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.75$, (d) $x = 1$ with temperatures from 25°C to 250°C ($\lambda_{ex}$ = 400 nm).