The stabilities of coordination polyhedrons and distributions of europium ions in $Ca_6BaP_4O_{17}$

Fengkai Ma[a], Rongfu Zhou[a], Fang Su[a], Yiyi Ou[a] and Hongbin Liang*[a]

[a]*MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, KLGHEI of Environment and Energy Chemistry, School of Chemistry, Sun Yat-sen University, Guangzhou, 510275, China*

**cesbin@mail.sysu.edu.cn*

Supporting Information

Table S1. Calculated atomic coordinates for the $Ca_6BaP_4O_{17}$ (CBPO) crystal using density functional theory (DFT) with the PAW_PBE (PBE) and USPP_LDA (LDA), and compared with the reported PAW_PBE0 (PBE0) and reference (REF) results.[1-2]

atom	site	methods	*x*	*y*	*z*
Ca1	4i	PBE	0.7163	0.0000	0.3087
		LDA	0.7176	0.0000	0.3111
		PBE0	0.7165	0.0000	0.3083
		REF	0.7194	0.0000	0.3117
Ca2	8j	PBE	0.0511	0.7669	0.6927
		LDA	0.0514	0.7679	0.6920
		PBE0	0.0509	0.7670	0.6924
		REF	0.0506	0.7666	0.6930
Ba	2a	PBE	0.0000	0.0000	0.0000
		LDA	0.0000	0.0000	0.0000
		PBE0	0.0000	0.0000	0.0000
		REF	0.0000	0.0000	0.0000
O10	2c	PBE	0.0000	0.0000	0.5000
		LDA	0.0000	0.0000	0.5000
		PBE0	0.0000	0.0000	0.5000
		REF	0.0000	0.0000	0.5000

O11	4i	PBE	0.3908	0.0000	0.5841
		LDA	0.3945	0.0000	0.5872
		PBE0	0.3900	0.0000	0.5835
		REF	0.4013	0.0000	0.5830
O12	8j	PBE	0.2870	-0.1781	0.3421
		LDA	0.2864	-0.1798	0.3411
		PBE0	0.2873	-0.1773	0.3428
		REF	0.2831	-0.1749	0.3364
O13	4i	PBE	0.1114	0.0000	0.3456
		LDA	0.1120	0.0000	0.3492
		PBE0	0.1115	0.0000	0.3447
		REF	0.1208	0.0000	0.3680
O21	4i	PBE	0.2919	0.0000	0.1139
		LDA	0.2916	0.0000	0.1155
		PBE0	0.2922	0.0000	0.1136
		REF	0.2877	0.0000	0.1077
O22	4i	PBE	0.2423	0.0000	-0.1371
		LDA	0.2424	0.0000	-0.1381
		PBE0	0.2425	0.0000	-0.1363
		REF	0.2432	0.0000	-0.1397
O23	8j	PBE	0.4680	-0.1762	0.1144
		LDA	0.4703	-0.1782	0.1172
		PBE0	0.4676	-0.1752	0.1140
		REF	0.4620	-0.1797	0.1148
P1	4i	PBE	0.2664	0.0000	0.3996
		LDA	0.2670	0.0000	0.4003
		PBE0	0.2664	0.0000	0.3996
		REF	0.2664	0.0000	0.3996
P2	4i	PBE	0.3658	0.0000	0.0487

LDA	0.3669	0.0000	0.0502
PBE0	0.3657	0.0000	0.0487
REF	0.3664	0.0000	0.0472

Table S2. Calculated unit cell dimensions for the CBPO crystal using DFT with the PBE and LDA, and compared with the reported PBE0 and REF results.[1-2]

Parameters	PBE	LDA	PBE0	REF
a (Å)	12.399	12.112	12.289	12.303
b (Å)	7.149	6.983	7.095	7.106
c (Å)	11.820	11.518	11.716	11.716
α (°)	90.000	90.000	90.000	90.000
β (°)	134.289	134.395	134.34	134.442
γ (°)	90.000	90.000	90.000	90.000
Volume (Å^3)	749.996	696.040	730.599	731.143

Table S3. Calculated bond lengths of divalent cations in CBPO using DFT with the PBE and LDA, and compared with the reported PBE0 and REF results.[1-2]

site	bond	distance (Å)			
		PBE	LDA	PBE0	REF
Ca1	Ca1–O10	2.526	2.454	2.499	2.473
	Ca1–O11	2.391	2.333	2.375	2.509
	Ca1–O12	2.395	2.326	2.381	2.390
	Ca1–O12	2.395	2.326	2.381	2.390
	Ca1–O13	3.012	2.876	2.997	2.760
	Ca1–O22	2.415	2.357	2.395	2.361
	Ca1–O23	2.543	2.479	2.520	2.598
	Ca1–O23	2.543	2.479	2.520	2.598
Ca2	Ca2–O10	2.520	2.445	2.497	2.506
	Ca2–O11	2.382	2.315	2.366	2.303

	Ca2–O12	2.399	2.330	2.382	2.392
	Ca2–O12	3.058	2.977	3.021	3.075
	Ca2–O13	2.402	2.336	2.386	2.366
	Ca2–O21	2.538	2.476	2.519	2.548
	Ca2–O22	2.405	2.340	2.387	2.388
	Ca2–O23	2.536	2.470	2.518	2.442
Ba	Ba–O12	3.247	3.158	3.218	3.160
	Ba–O12	3.247	3.158	3.218	3.160
	Ba–O12	3.247	3.158	3.218	3.160
	Ba–O12	3.247	3.158	3.218	3.160
	Ba–O13	3.274	3.222	3.233	3.438
	Ba–O13	3.274	3.222	3.233	3.438
	Ba–O21	2.847	2.769	2.826	2.804
	Ba–O21	2.847	2.769	2.826	2.804
	Ba–O23	2.845	2.771	2.828	2.844
	Ba–O23	2.845	2.771	2.828	2.844
	Ba–O23	2.845	2.771	2.828	2.844
	Ba–O23	2.845	2.771	2.828	2.844

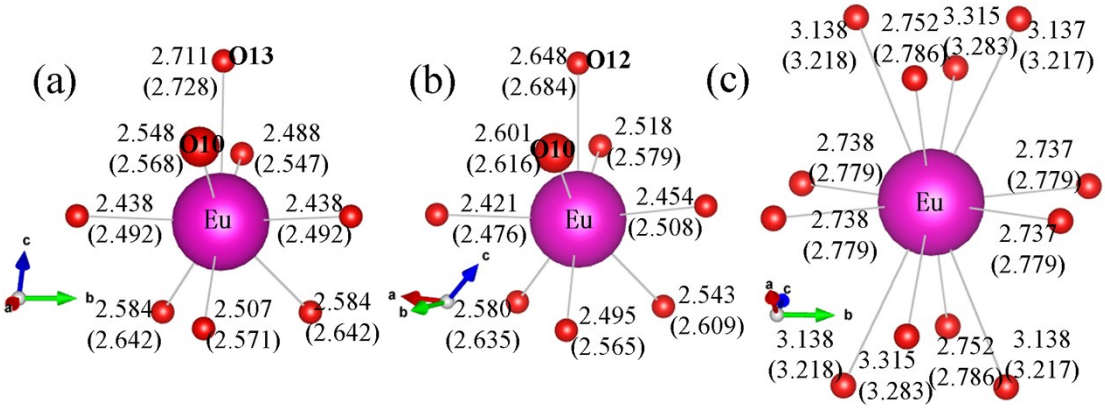

Fig. S1. Coordination geometries of Eu^{2+} occupied the Ca1 (a), Ca2 (b) and Ba site (c) relaxed with the potentials of Eu_2 (Eu), in Eu_2 potential the orbitals of $5p^6 6s^2$ are treated as the valence electrons, and in Eu potential the $5s^2 5p^6 4f^7 6s^2$ are as the valence electrons in the calculation. Bond length is in unit of Å.

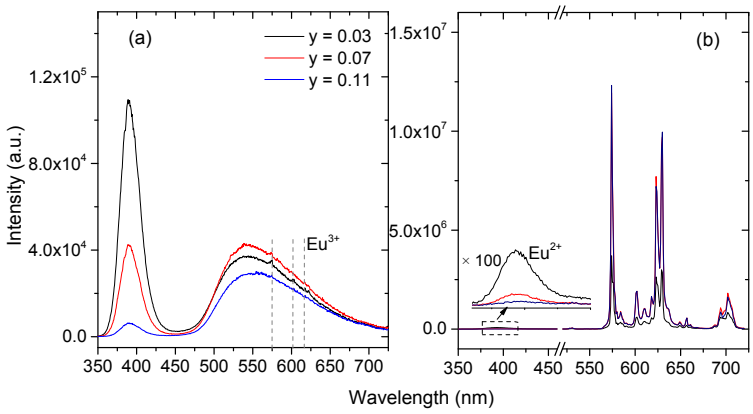

Fig. S2 Room temperature emission spectra of europium-doped CBPO prepared in the reducing ambience (a) and in the air (b), the FLS1000 fluorimeter is used with excitation of a 450 W xenon lamp at 300 nm. The dotted weak sharp lines in (a) are the 4f – 4f transitions of Eu^{3+}, and weak broad ones in (b) the 4f – 5d transitions of Eu^{2+}.

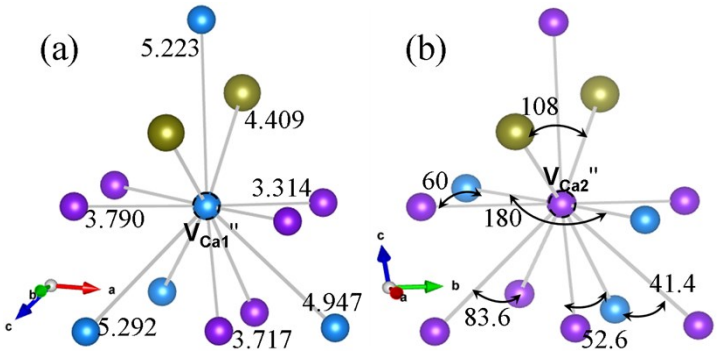

Fig. S3. Divalent cations coordinated structure of Ca1 with maximum bond distance of 5.292 Å, the first cationic shell of Ca1 ion for clear view (a), and of Ca2 site with maximum angle of 180 ° (b). The dotted circles of Ca1 and Ca2 mean that they are vacancies of V_{Ca1}'' and V_{Ca2}'', respectively.

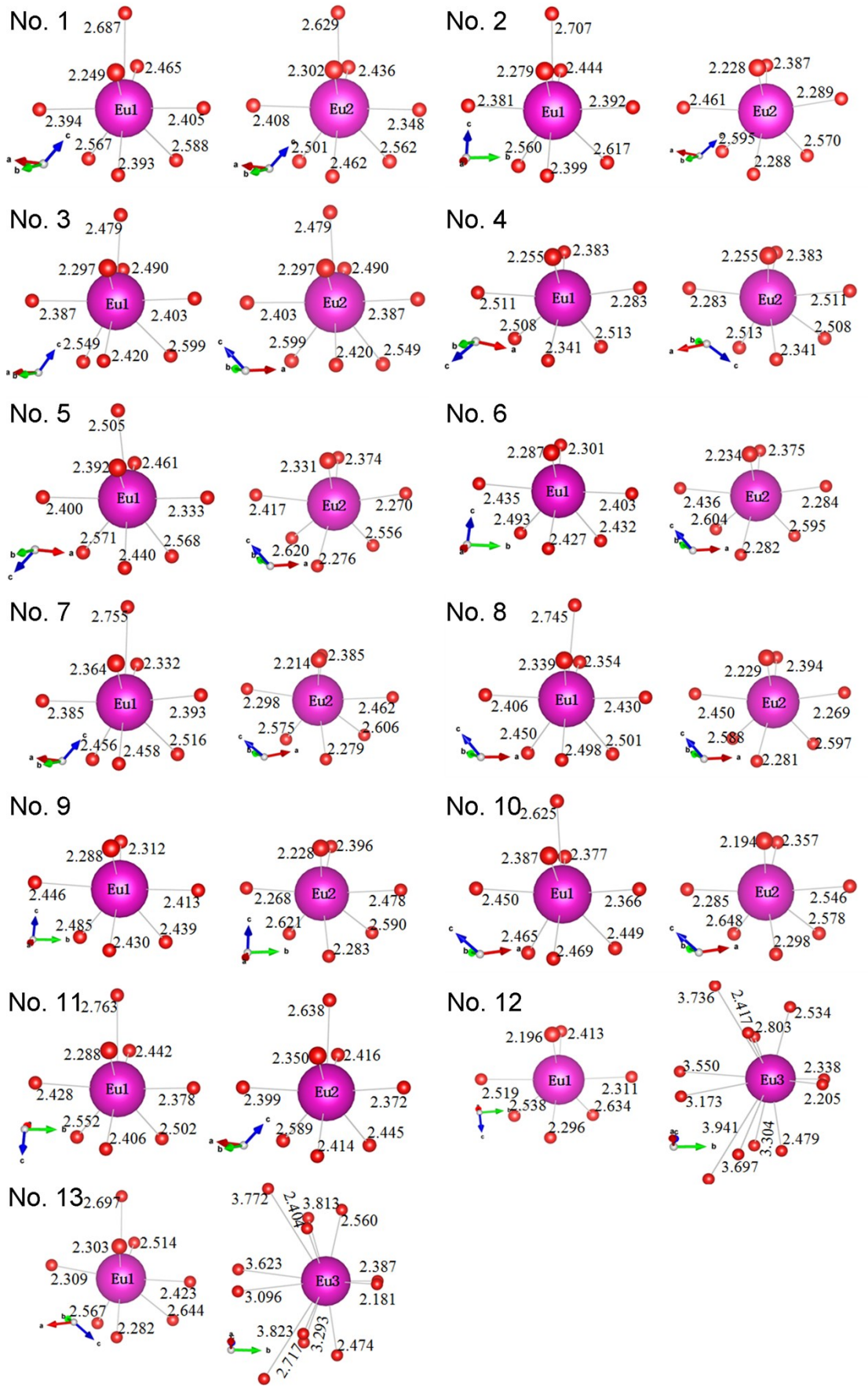

Fig. S4. Relaxed coordination geometries of two Eu^{3+} at the divalent cationic sites

with a $V_{Ca/Ba}$" vacancy. Nos. 1–13 are case numbers of defect. Eu1 and Eu2 occupy the Ca site, and Eu3 at Ba site. Bond length is in unit of Å.

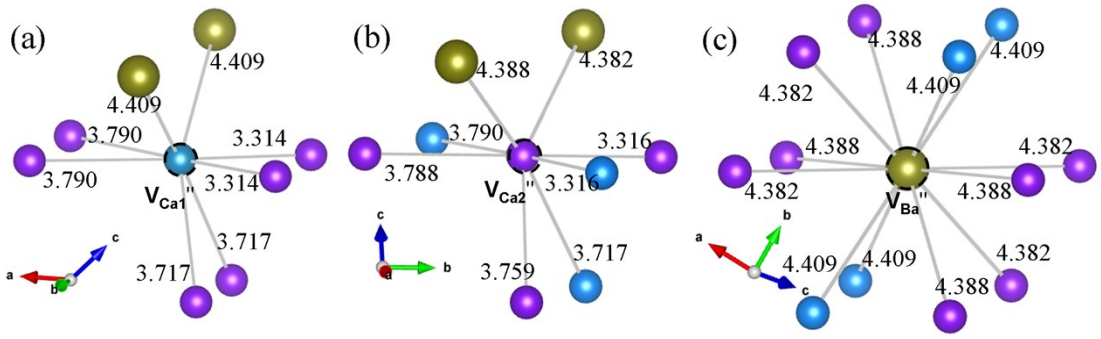

Fig. S5. The nearest divalent cations coordinated structure of Ca1 with maximum bond distance of 4.409 Å (a), of Ca2 with 4.388 Å (b) and of Ba with 4.409 Å (c). The dotted circles of Ca1, Ca2 and Ba mean that they are vacancies of V_{Ca1}", V_{Ca2}" and V_{Ba}", respectively.

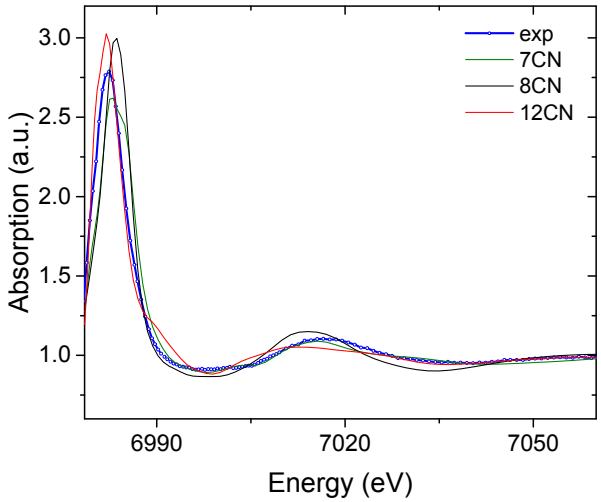

Fig. S6. Calculated XANES spectra of Eu^{3+} in the sites of 7CN, 8CN and 12CN, and compared with the experiment line of CBPO: Eu^{3+} (y = 0.07).

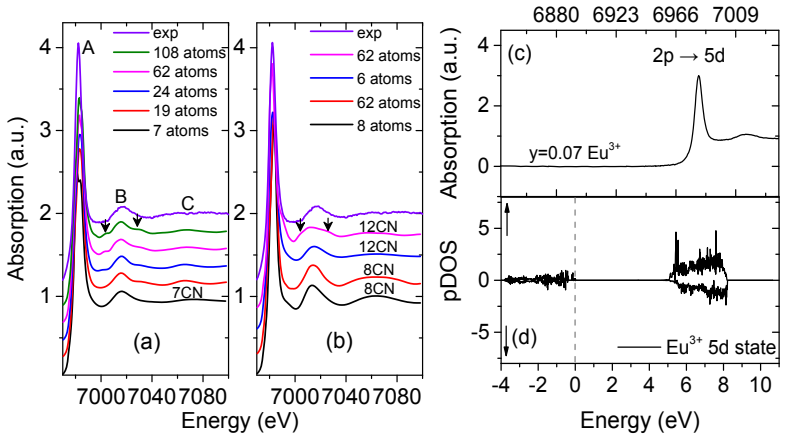

Fig. S7. Calculated XANES spectra of 7CN (a), 8CN and 12CN (b) with varied cluster sizes and compared with the experimental line, A, B, C and arrows denoted the peaks; (c) and (d) respectively the absorption spectra of CBPO: Eu^{3+} (y = 0.07) and pDOS of 5d state. Dotted line is the Fermi level.

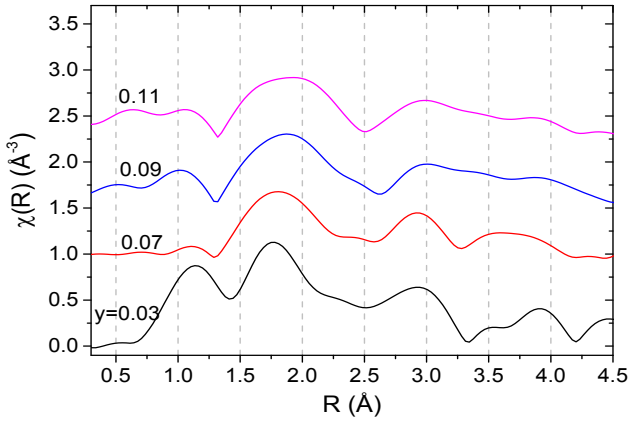

Fig. S8. Pair distribution function (PDF) of CBPO: Eu^{3+} with no phase correction.

Table S4. The varied bond length of $Eu1_{Ca1}$–O13 in center No. 6, and the corresponding averaged bond length of first anionic shell of Eu^{3+} at the site of Ca1.

Bond length (Å)		
$Eu1_{Ca1}$–	ABL	
O13	7CN	8CN
2.674		2.461

2.876		2.473
3.076	2.404	2.488
3.176	2.399	
3.228	2.397	
3.329	2.394	
3.379	2.392	

References

[1] L.X. Ning, X.X. Huang, J.C. Sun, S.Z. Huang, M.Y. Chen, Z.G. Xia, Y.C. Huang, Effects of Si codoping on optical properties of Ce-doped $Ca_6BaP_4O_{17}$: insights from first-principles calculations, J. Phys. Chem. C 120 (2016) 3999-4006. https://doi.org/10.1021/acs.jpcc.5b11659.

[2] N. Komuro, M. Mikami, Y. Shimomura, E.G. Bithell, A.K. Cheetham, Synthesis, structure and optical properties of europium doped calcium barium phosphate-a novel phosphor for solid-state lighting, J. Mater. Chem. C 2 (2014) 6084-6089. https://doi.org/10.1039/C4TC00732H.