Supporting Information for:

Origin of the Abnormal Reduction of the Dielectric Response for ReCOB Crystals and its Mechanism: Theoretical and Experimental Exploration

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Table S1 Bond lengths (Å) and angles (deg.) of ReO_6, $Ca1O_6$ and $Ca2O_6$ polyhedrons in YCOB, PrCOB, and LaCOB crystals.

Figure S1 Calculated band gaps of YCOB(a1-a3), PrCOB(b), and LaCOB(c1,c2) as a function of U_{eff}. The red points correspond to the U_{eff} for *d* or *f* orbitals of rare earth ions, while the blue points correspond to the U_{eff} including O 2*p* states.

Figure S2 Partial density of states (PDOSs) of YCOB (a), PrCOB (b), and LaCOB (c) within GGA-PBE, HSE06 and GGA+U methods.

Figure S3 Density of states of decomposed Pr 4f orbitals (left) and the structural of PrO6 (right).

Table S2 Atomic coordinates and equivalent isotropic displacement for ReCOB (Re = Y, Pr, La). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S3 Calculated dielectric constants (ε_{ij}), and their electronic ($\varepsilon_{\infty,ij}$) and phonon ($\varepsilon_{ph,ij}$) contributions for the neutral defects in ReCOB and the charged defects in LaCOB. The calculated values for the pristine crystals and the experimental values are also listed for comparison.

Table S1 Bond lengths (Å) and angles (deg.) of ReO_6, $Ca1O_6$ and $Ca2O_6$ octahedrons in YCOB, PrCOB, and LaCOB crystals.

ReO_6	Re-O1	Re-O2	∠O1ReO2	Re-O4	∠O4ReO4	r^{Re}(+3)
YCOB	2.26 /2.22	2.15	177.73 /80.05	2.26	139.31	0.900
PrCOB	2.40 /2.34	2.24	177.01 /82.40	2.40	135.50	0.990
LaCOB	2.43 /2.36	2.24	176.65 /82.34	2.41	135.57	1.032

$Ca1O_6$	Ca1-O4	Ca1-O5	∠O4Ca1O5	Ca1-O3	Ca1-O6	∠O3Ca1O6
YCOB	2.24 /2.21	2.63 /2.31	174.65 /84.64	2.24	2.33	129.30
PrCOB	2.24 /2.20	2.60 /2.30	176.60 /81.34	2.25	2.39	128.99
LaCOB	2.24 /2.21	2.58/ 2.30	176.92 /80.90	2.25	2.40	128.75

$Ca2O_6$	Ca2-O3	Ca2-O6	∠O3Ca2O6	Ca2-O2	Ca2-O5	∠O2Ca2O5
YCOB	2.23 /2.21	2.26 /2.23	169.04 /81.64	2.18	2.23	171.72
PrCOB	2.26 /2.22	2.30 /2.25	173.56 /80.49	2.17	2.23	174.14
LaCOB	2.27 /2.23	2.32 /2.25	173.89 /80.33	2.17	2.23	174.53

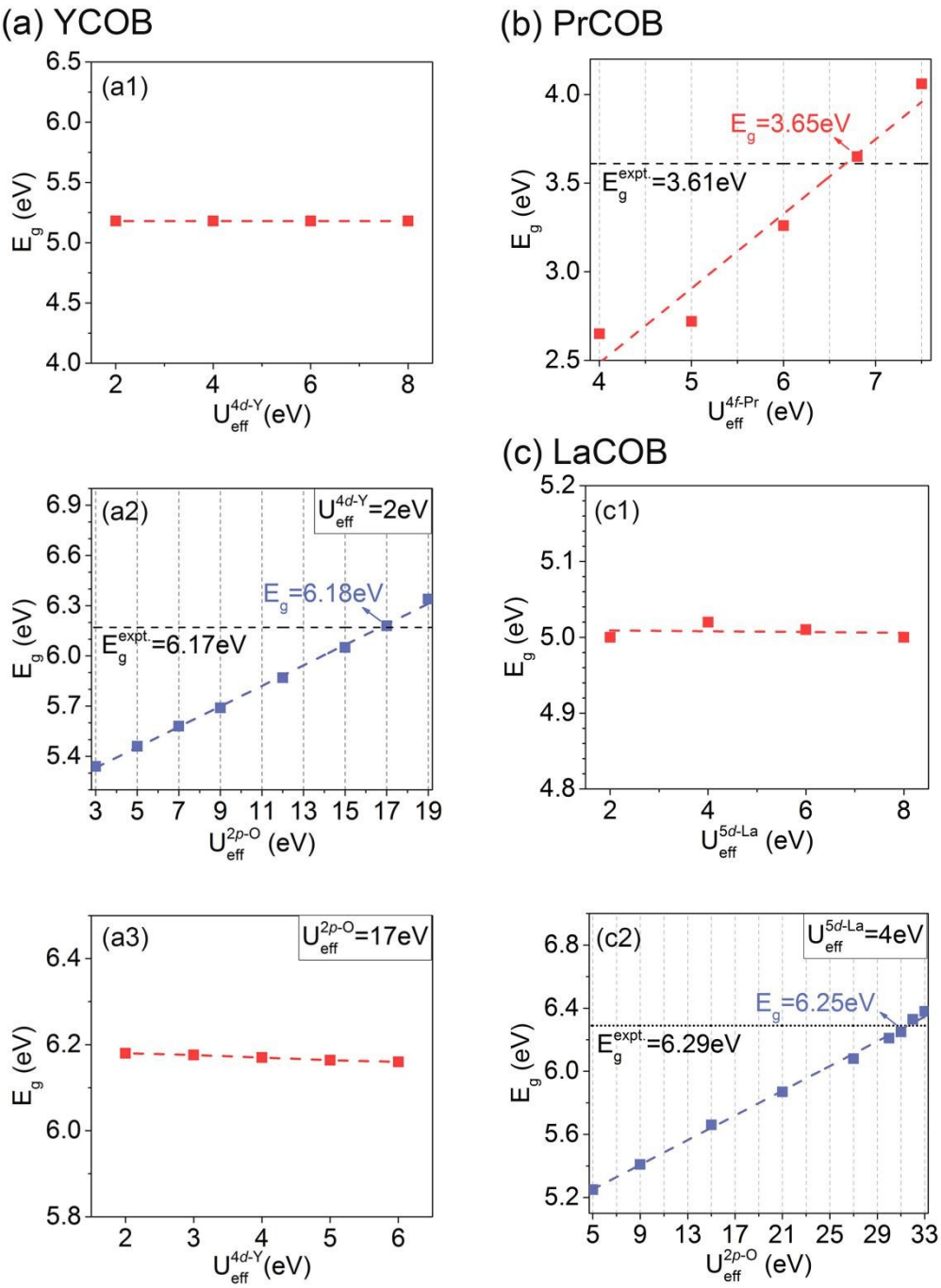

Figure S1 Calculated band gaps of YCOB(a1-a3), PrCOB(b), and LaCOB(c1,c2) as a function of U_{eff}. The red points correspond to the U_{eff} for *d* or *f* orbitals of rare earth ions, while the blue points correspond to the U_{eff} including O 2*p* states.

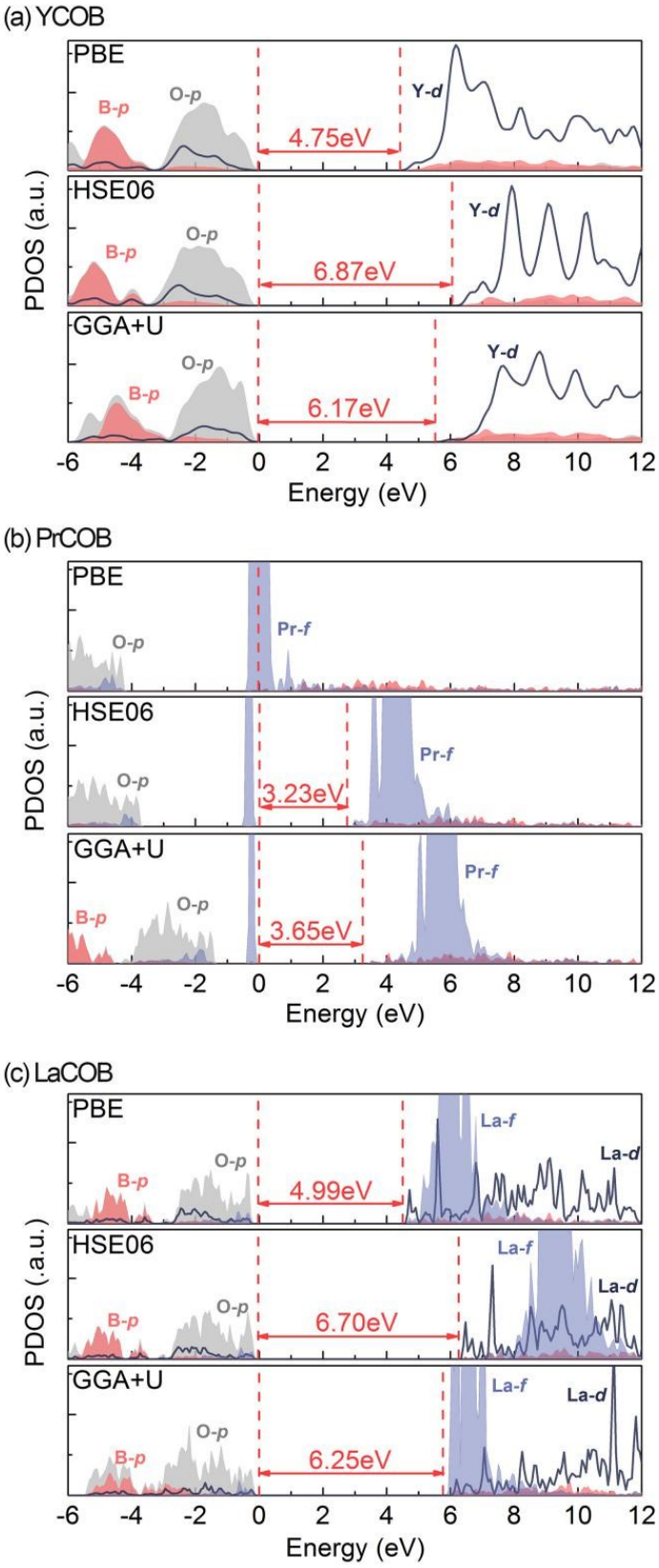

Figure S2 Partial density of states (PDOSs) of YCOB (a), PrCOB (b), and LaCOB (c) within GGA-PBE, HSE06 and GGA+U methods.

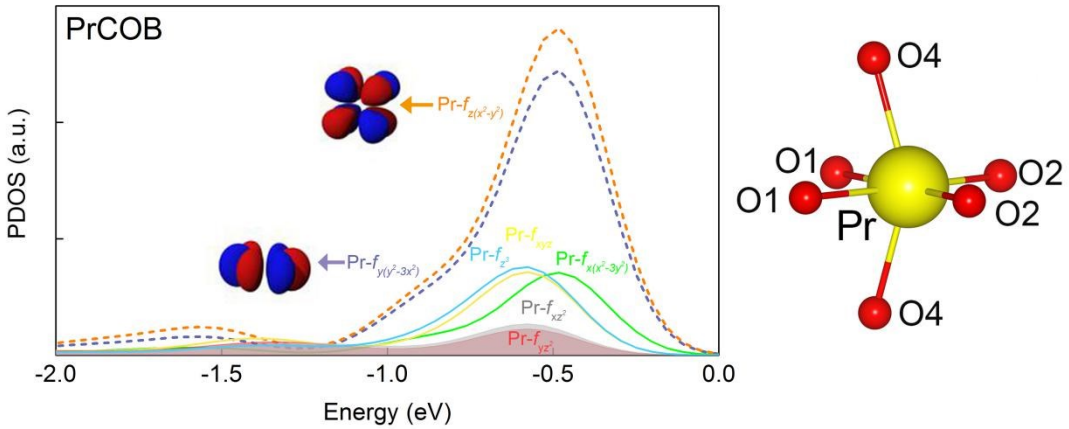

Figure S3 Density of states of decomposed Pr 4f orbitals (left) and the structural of PrO6 (right).

Table S2 Atomic coordinates and equivalent isotropic displacement for ReCOB (Re = Y, Pr, La). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
		$YCa_4O(BO_3)_3$		
L*	0.1703(8)	0.5000	0.1253(14)	0.004(15)
M*	0.5310(10)	0.3877(5)	-0.1991(19)	0.004(19)
Ca(1)	-0.0863(11)	0.3186(6)	0.4776(2)	0.006(2)
O (1)	-0.0253(6)	0.5000	0.5259(13)	0.009(11)
O (2)	0.3445(6)	0.5000	0.7094(14)	0.006(9)
O (3)	0.7117(4)	0.4256(19)	-0.6210(8)	0.007(7)
O (4)	0.0909(4)	0.3589(19)	0.0569(8)	0.006(6)
O (5)	0.7028(4)	0.2691(19)	-0.1498(8)	0.008(6)
O (6)	0.3852(4)	0.3259(18)	0.2475(8)	0.007(6)
B (1)	-0.1992(9)	0.5000	0.4300(2)	0.004(13)
B (2)	0.2257(7)	0.3055(3)	0.0506(14)	0.005(10)

**L=0.87Y+0.13Ca;M=0.07Y+0.93Ca*

		$PrCa_4O(BO_3)_3$		
Pr	0.3593(3)	0.5000	0.1535(4)	0.008(9)
Ca(1)	0.6284(9)	0.3187(5)	-0.1839(19)	0.010(17)
Ca(2)	0.0041(9)	0.3863(4)	0.4858(19)	0.007(17)
O (1)	0.5686(6)	0.5000	-0.2363(14)	0.014(12)
O (2)	0.1843(6)	0.5000	0.5679(13)	0.006(9)
O (3)	0.8276(3)	0.5739(16)	-0.0899(7)	0.011(6)
O (4)	0.455(3)	0.3542(17)	0.2405(8)	0.011(6)
O (5)	0.3290(3)	0.2304(16)	0.4338(7)	0.013(6)
O (6)	0.6613(3)	0.1700(16)	0.0449(7)	0.012(6)
B (1)	0.7427(7)	0.5000	-0.1379(16)	0.008(12)
B (2)	0.3146(5)	0.3057(3)	0.2408(12)	0.007(8)

$LaCa_4O(BO_3)_3$				
L*	0.3380(4)	0.5000	0.1699(5)	0.010(12)
M*	0.0660(10)	0.3196(5)	0.5030(2)	0.012(3)
Ca(1)	0.6911(10)	0.3860(5)	-0.1650(2)	0.007(2)
O (1)	0.1228(6)	0.5000	0.5602(15)	0.016(13)
O (2)	0.5157(6)	0.5000	-0.2453(15)	0.010(11)
O (3)	0.8650(4)	0.4257(17)	-0.5898(8)	0.012(6)
O (4)	0.2386(4)	0.3524(18)	0.0782(8)	0.013(7)
O (5)	0.3683(4)	0.2295(17)	-0.1104(8)	0.015(6)
O (6)	0.5320(4)	0.3307(18)	0.2749(8)	0.014(7)
B (1)	0.9493(8)	0.5000	-0.5415(17)	0.006(13)
B (2)	0.3799(6)	0.3049(3)	0.0806(12)	0.008(9)

**L=0.96La+0.04Ca;M=0.02La+0.98Ca*

Table S3 Calculated dielectric constants (ε_{ij}), and their electronic ($\varepsilon_{\infty,ij}$) and phonon ($\varepsilon_{ph,ij}$) contributions for the neutral defects in ReCOB and the charged defects in LaCOB. The calculated values for the pristine crystals and the experimental values are also listed for comparison.

			ij		
			11	22	33
YCOB					
	Ca_Y	$\varepsilon_{\infty,ij}$	2.31	2.31	2.26
		$\varepsilon_{ph,ij}$	6.92	9.49	7.23
		ε_{ij}	9.23	11.80	9.49
	Y_{Ca2}	$\varepsilon_{\infty,ij}$	3.55	3.74	2.98
		$\varepsilon_{ph,ij}$	6.93	8.80	6.66
		ε_{ij}	10.48	12.54	9.64
	Pristine		8.10	9.74	7.72
	Expt.		9.65	12.00	9.55
PrCOB					
	Ca_{Pr}	$\varepsilon_{\infty,ij}$	3.89	3.43	3.45
		$\varepsilon_{ph,ij}$	4.81	7.35	6.06
		ε_{ij}	8.70	10.78	9.51
	Pr_{Ca1}	$\varepsilon_{\infty,ij}$	4.92	4.82	3.94
		$\varepsilon_{ph,ij}$	6.58	11.70	7.55
		ε_{ij}	11.50	16.52	11.49
	Pr_{Ca2}	$\varepsilon_{\infty,ij}$	4.19	3.86	3.72
		$\varepsilon_{ph,ij}$	5.95	6.88	5.47
		ε_{ij}	10.14	10.74	9.19
	Pristine		9.25	16.69	8.41
	Expt.		9.60	15.30	10.00
LaCOB					
Neutral	Ca_{La}	$\varepsilon_{\infty,ij}$	2.57	2.57	2.58

		$\varepsilon_{ph,ij}$	9.22	15.78	11.04
		ε_{ij}	11.79	18.35	13.62
	La_{Ca1}	$\varepsilon_{\infty,ij}$	2.95	2.87	2.85
		$\varepsilon_{ph,ij}$	5.37	6.51	5.31
		ε_{ij}	8.32	9.38	8.16
	La_{Ca2}	$\varepsilon_{\infty,ij}$	3.93	3.18	3.09
		$\varepsilon_{ph,ij}$	8.65	8.69	6.48
		ε_{ij}	12.58	11.87	9.57
Charged	Ca_{La}^{-}	$\varepsilon_{\infty,ij}$	2.63	2.69	2.61
		$\varepsilon_{ph,ij}$	9.52	14.67	13.72
		ε_{ij}	12.15	17.36	16.33
	La_{Ca1}^{+}	$\varepsilon_{\infty,ij}$	2.60	2.61	2.60
		$\varepsilon_{ph,ij}$	8.78	12.27	10.09
		ε_{ij}	11.38	14.88	12.69
	La_{Ca2}^{+}	$\varepsilon_{\infty,ij}$	2.60	2.61	2.59
		$\varepsilon_{ph,ij}$	9.15	12.73	10.13
		ε_{ij}	11.75	15.34	12.72
Pristine			8.68	10.26	8.24
Expt.			9.40	15.00	9.60