Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Figures and Tables

1. Projected Density of States

The projected density of states for defect formation of Y_{Ba}, Y_{Fe} Ce_{Ba}, and Ce_{Fe} defects in BFO, shows similar trends to defect formation in La_{Ba} and La_{Fe} structures. Specifically, A_{Ba} defects are show a shift in the Fermi level of the O 2p states to higher energies, suggesting hole reduction B_{Fe} defects show little effect on O 2p states.

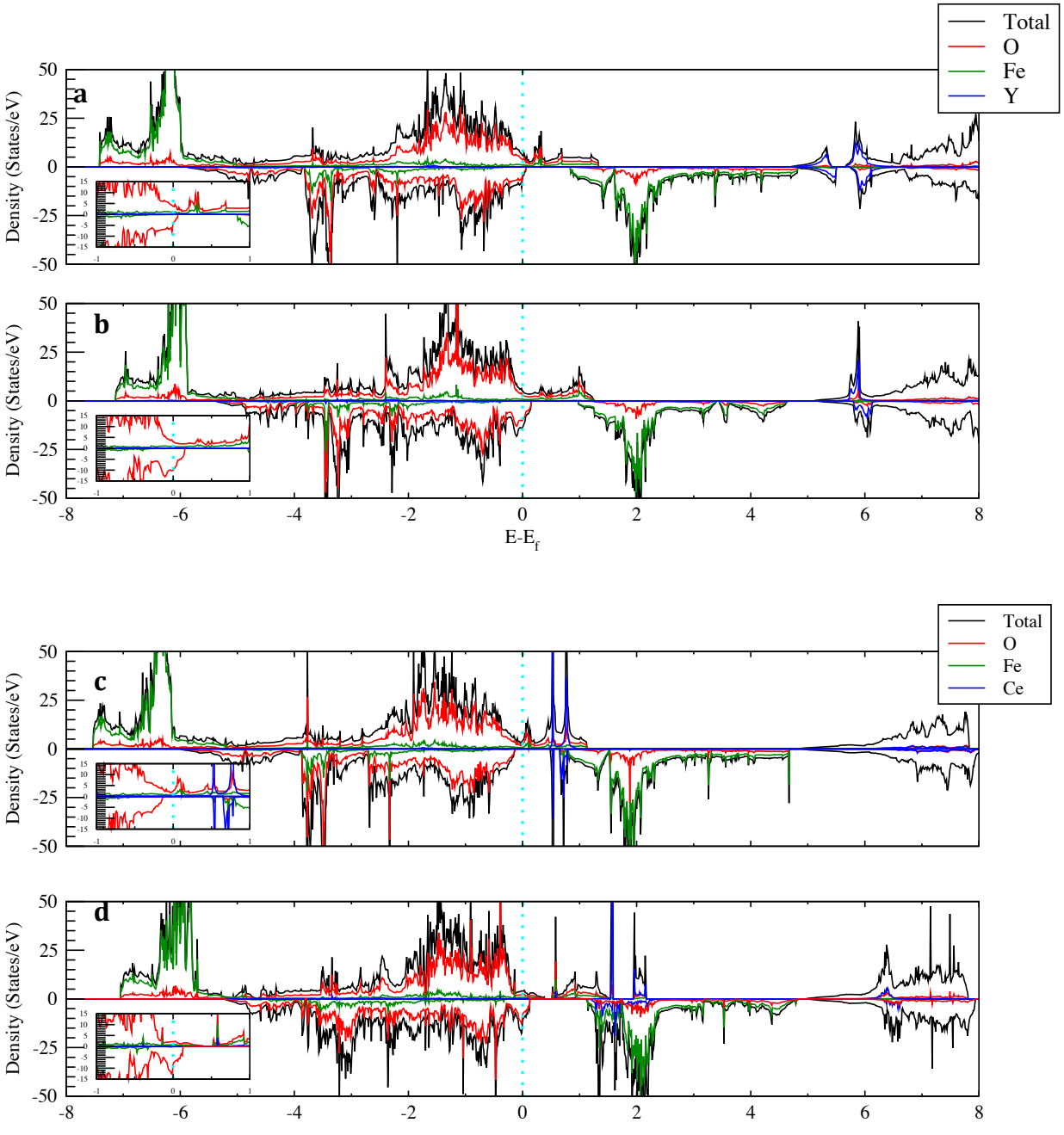

Figure S1 Projected Fe, O ,Y & Ce, and total density of states of $BaFeO_3$ with a) Y_{Ba} , b) Y_{Fe}, c) Ce_{Ba} and, d) Ce_{Fe} substitutions. The dashed cyan line corresponds to Fermi energy and insets show Fermi-level detail.

2. Bader Charge Analysis for Oxygen Vacancy formation

Bader charge analysis of oxygen vacancy formation for all Ce_{Ba}, Ce_{Fe}, Y_{Ba} and Y_{Fe} defects in BFO, shows a the same trend for charge redistribution with oxygen vacancy formation as observed for La_{Ba} and La_{Fe} structures. That is, a predominant localisation of additional charge to O sub-lattice for B_{Fe} defects, and significant localisation of dopant charge to A-manifold for A_{Ba} defects

Table S1. Bader charge $q(e)$, Magnetic moment of Fe $\mu_{Fe}(\mu_B)$ for the stoichiometric structures of BFO and BFO with Ce_{Ba} , Ce_{Fe} , Y_{Ba} and Y_{Fe} defects. δ=0 corresponds to stoichiometric structure and δ=0.125 corresponds to a single oxygen vacancy. To note Bader chargers for oxygen vacancy structures, are for the optimum oxygen vacancy sites, as discussed in the manuscript.

	Ce_{Ba}		Ce_{Fe}		Y_{Ba}		Y_{Fe}	
Property	δ = 0	δ = 0.125	δ = 0	δ = 0.125	δ = 0	δ = 0.125	δ = 0	δ = 0.125
μ_{Fe} [a]	3.92	4.05	3.77	3.82	3.88	4.00	3.79	3.88
μ_{Fe*} [a,b]	---	3.81	---	3.85	---	3.74	---	3.54
q_{Fe} [a]	1.83	1.82	1.74	1.76	1.83	1.79	1.70	1.75
q_{Fe*} [a,b]	---	1.68	---	1.71	---	1.67	---	1.76
q_{Ba} [a]	1.59	1.55	1.57	1.56	1.58	1.55	1.59	2.56
$q_{A/B}$ [a]	2.20	2.38	2.26	2.26	2.21	2.54	2.12	2.13
q_O [a]	-1.16	-1.20	-1.12	-1.17	-1.17	-1.18	-1.11	-1.17

[a] To note Bader chargers for oxygen vacancy structures, are for the optimum oxygen vacancy sites, as discussed in the manuscript. [b] Fe* indicates the Fe ions adjacent to the vacancy.