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

Electronic Supporting Information

A DFT+*U* study on the contribution of 4f electrons to oxygen vacancy formation and migration in Ln-doped CeO_2

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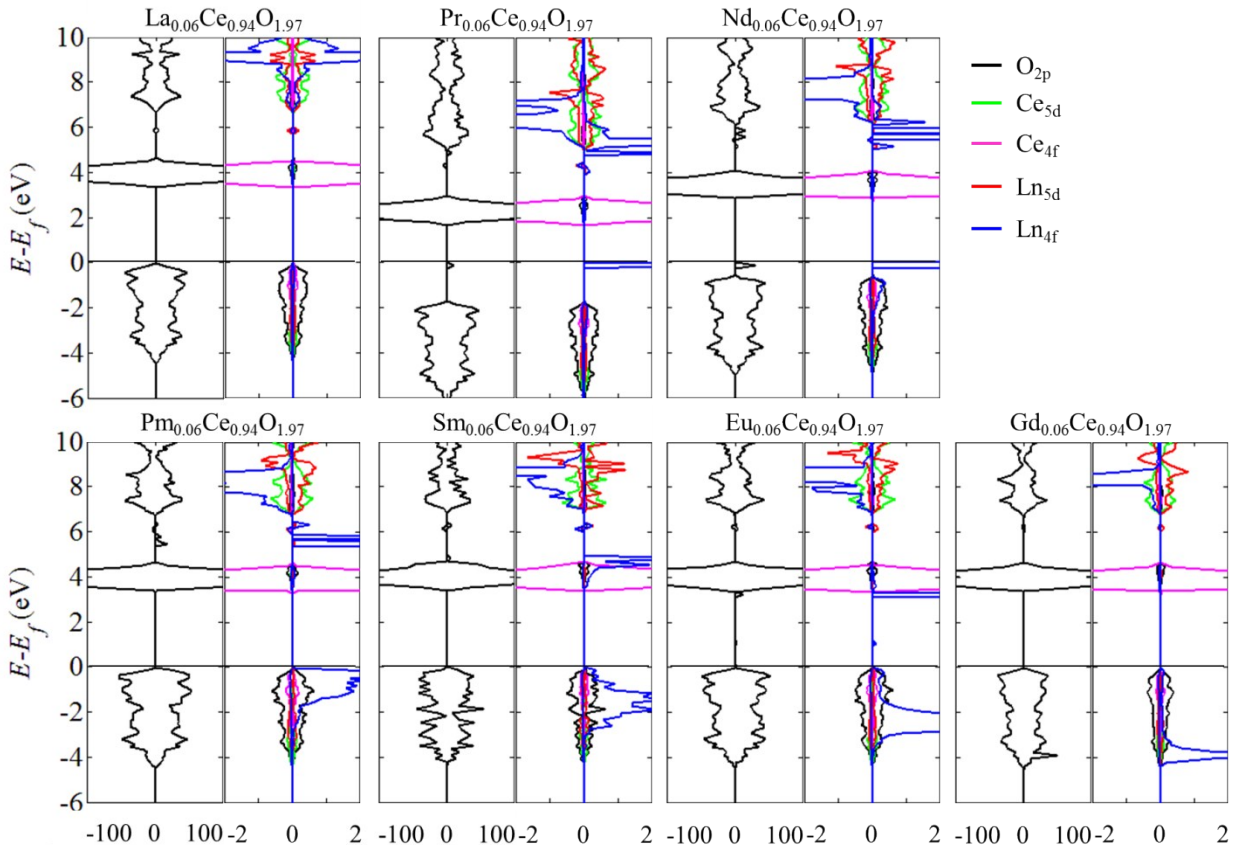

Figure S1. Total DOS and projected DOS obtained from hybrid functional calculations [1].

Table S1. The vacancy formation energies, E_f^{vac}, and migration energies, $\Delta E_{m,}$ for ip1, ip2, and ip3. The calculations were conducted by considering 4f electrons frozen at the core ($Ln_{4f@core}$) and as valence electrons with $U_{eff@Ln}$ = 0 eV as well as with the fitted $U_{eff@Ln}$ specified in the computational details section in the main manuscript.

Systems	Ln_{4f} Treatment	ΔE_m (eV)			E_f^{vac} (eV)
		ip1(fwd/bwd)	ip2(fwd/bwd)	ip3(fwd/bwd)	
LCO	$U_{eff@La}$ = 0 eV	0.338/0.424	0.811/0.782	1.591/1.591	-0.614
	$U_{eff@La}$ = 4.5 eV	0.305/0.465	0.794/0.811	1.695/1.695	-0.662
CeO_{2-x}	$U_{eff@Ce}$* = 5 eV		0.442/0.442		3.693
	$Ce_{4f@core}$**	0.370/0.486	0.798/0.809	1.629/1.629	4.546
PCO	$U_{eff@Pr}$ = 0 eV	0.534/0.333	0.395/0.330	0.968/0.968	3.127
	$U_{eff@Pr}$ = 4 eV	0.466/0.414	0.810/0.746	1.361/1.361	1.640
	$Pr_{4f@core}$	0.437/0.464	0.801/0.771	1.356/1.356	-0.590
NCO	$U_{eff@Nd}$ = 0 eV	0.536/0.366	0.700/0.662	0.898/0.898	1.077
	$U_{eff@Nd}$ = 3.5 eV	0.497/0.431	0.788/0.747	1.325/1.325	-0.100
	$Nd_{4f@core}$	0.501/0.447	0.799/0.740	1.373/1.373	-0.608
PmCO	$U_{eff@Pm}$ = 0 eV	0.585/0.373	0.831/0.697	1.171/1.171	0.683
	$U_{eff@Pm}$ = 3.5 eV	0.544/0.391	0.827/0.718	1.293/1.293	-0.581
	$Pm_{4f@core}$	0.574/0.430	0.793/0.700	1.256/1.256	-0.656
SCO	$U_{eff@Sm}$ = 0 eV	0.591/0.392	0.776/0.654	1.001/1.001	0.360
	$U_{eff@Sm}$ = 4 eV	0.578/0.425	0.814/0.710	1.193/1.193	-0.622
	$Sm_{4f@core}$	0.612/0.404	0.788/0.669	1.189/1.189	-0.697
ECO	$U_{eff@Eu}$ = 0 eV	0.571/0.389	0.836/0.714	1.068/1.068	-0.293
	$U_{eff@Eu}$ = 4 eV	0.598/0.435	0.839/0.730	1.230/1.230	-0.650
GCO	$U_{eff@Gd}$ = 0 eV	0.723/0.337	0.775/0.575	1.015/1.015	-0.636
	$U_{eff@Gd}$ = 4 eV	0.708/0.355	0.774/0.590	1.039/1.039	-0.793
	$Gd_{4f@core}$	0.734/0.363	0.766/0.576	1.018/1.018	-0.793
YCO	--	0.818/0.316	0.750/0.503	0.906/0.906	-0.891

* U_{eff} = 5 eV for all Ce 4f-electrons.

** The 4f-electrons of two reduced Ce ions as virtual dopants in the presence of an oxygen vacancy, are set as core electrons.

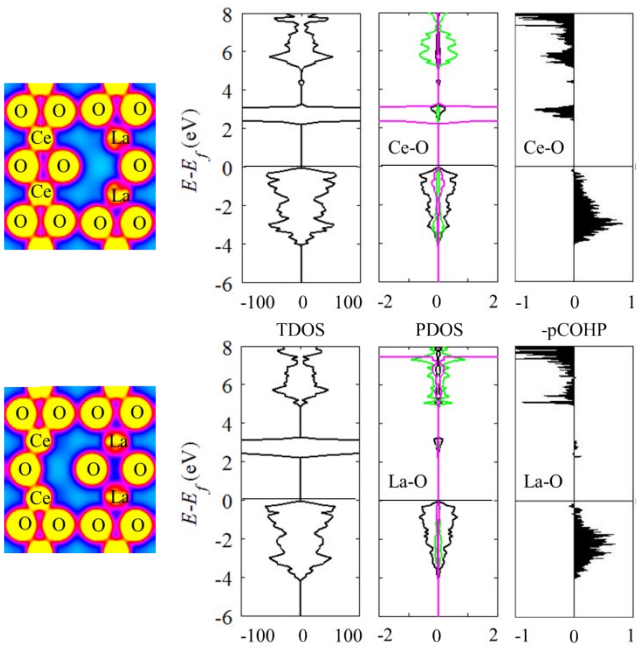

Figure S2. Charge density plots within energy range of O_{2p}-VB, total and projected DOS and the corresponding COHP curves of La-doped CeO_2 at initial and final states of ip1.

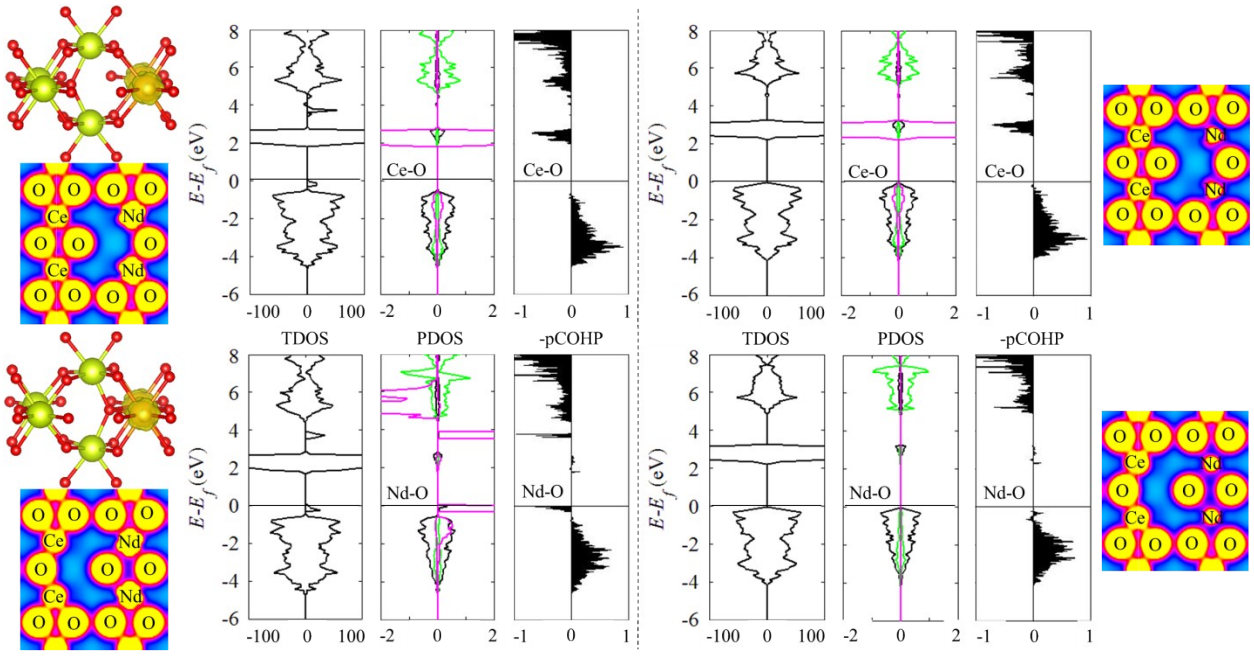

Figure S3. Charge density plots within energy range of O_{2p}-VB, total and projected DOS and the corresponding COHP curves of Nd-doped CeO_2 at initial and final states of ip1. Left panel shows the 4fval results while right panel shows the 4fcore results.

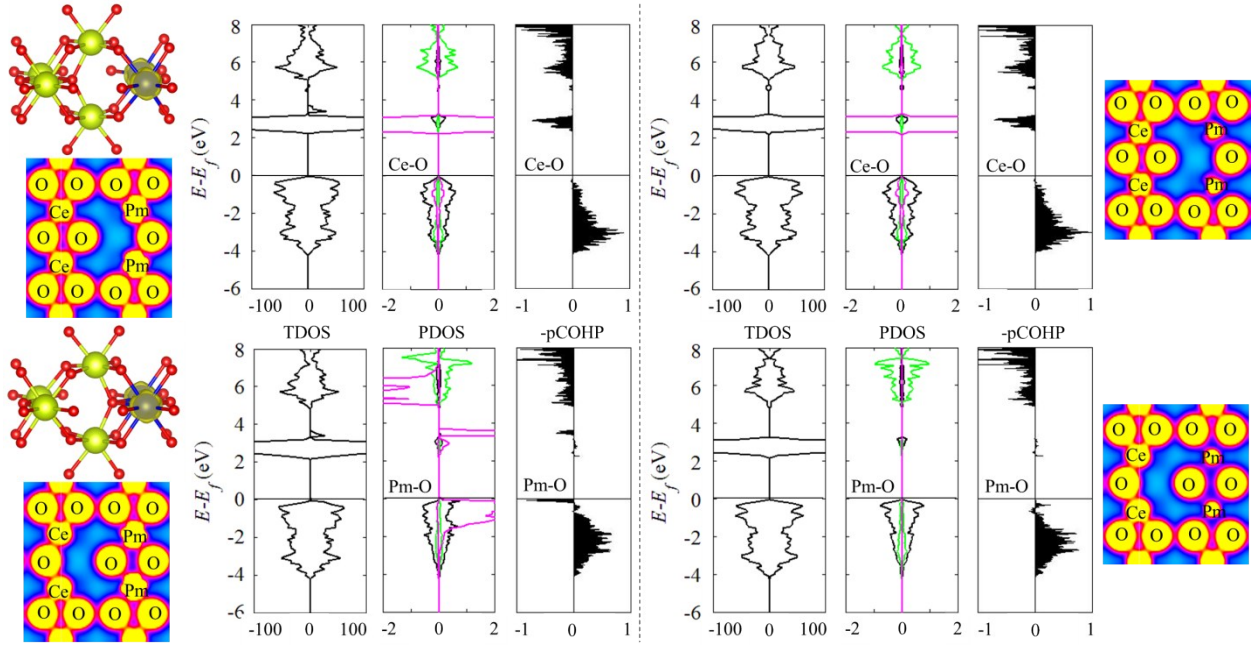

Figure S4. Charge density plots within energy range of O_{2p}-VB, total and projected DOS and the corresponding COHP curves of Pm-doped CeO_2 at initial and final states of ip1. Left panel shows the 4fval results while right panel shows the 4fcore results.

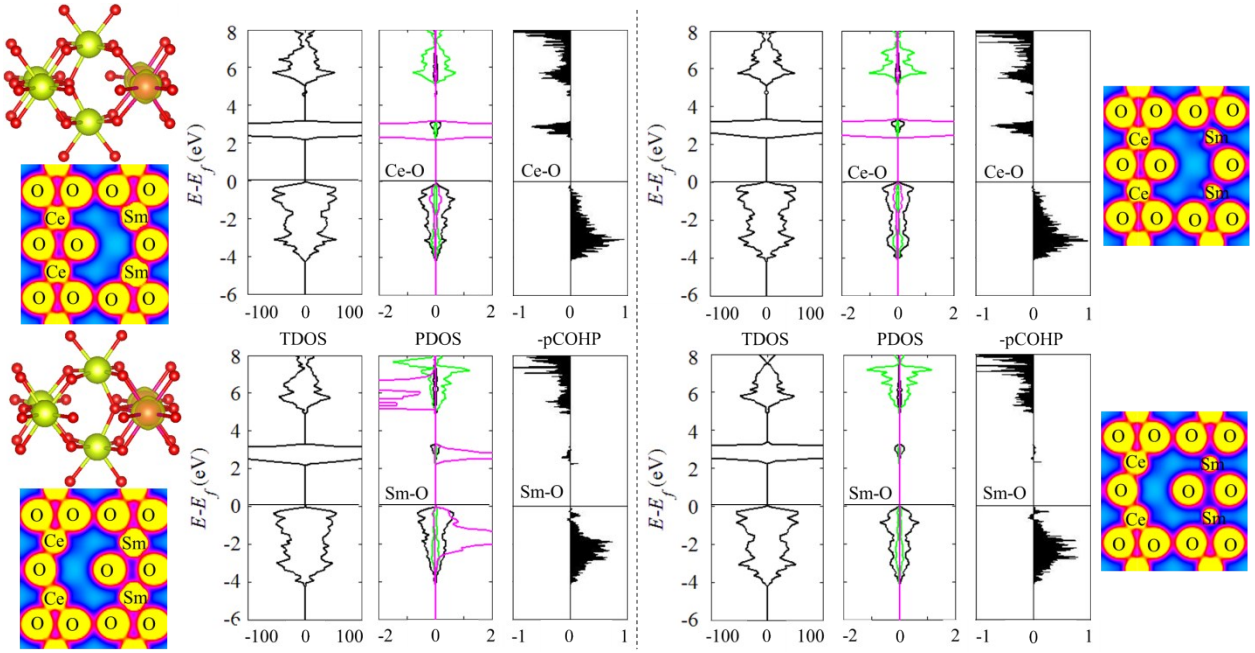

Figure S5. Charge density plots within energy range of O_{2p}-VB, total and projected DOS and the corresponding COHP curves of Sm-doped CeO_2 at initial and final states of ip1. Left panel shows the 4fval results while right panel shows the 4fcore results.

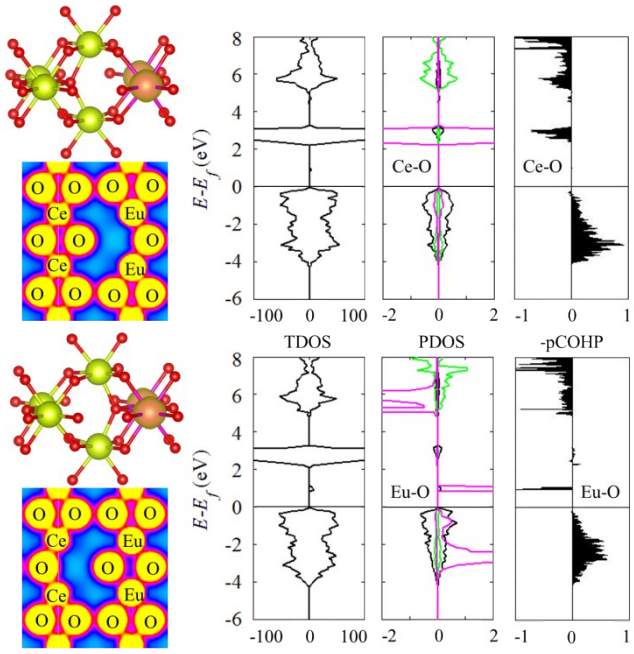

Figure S6. Charge density plots within energy range of O_{2p}-VB, total and projected DOS and the corresponding COHP curves of Eu-doped CeO_2 at initial and final states of ip1.

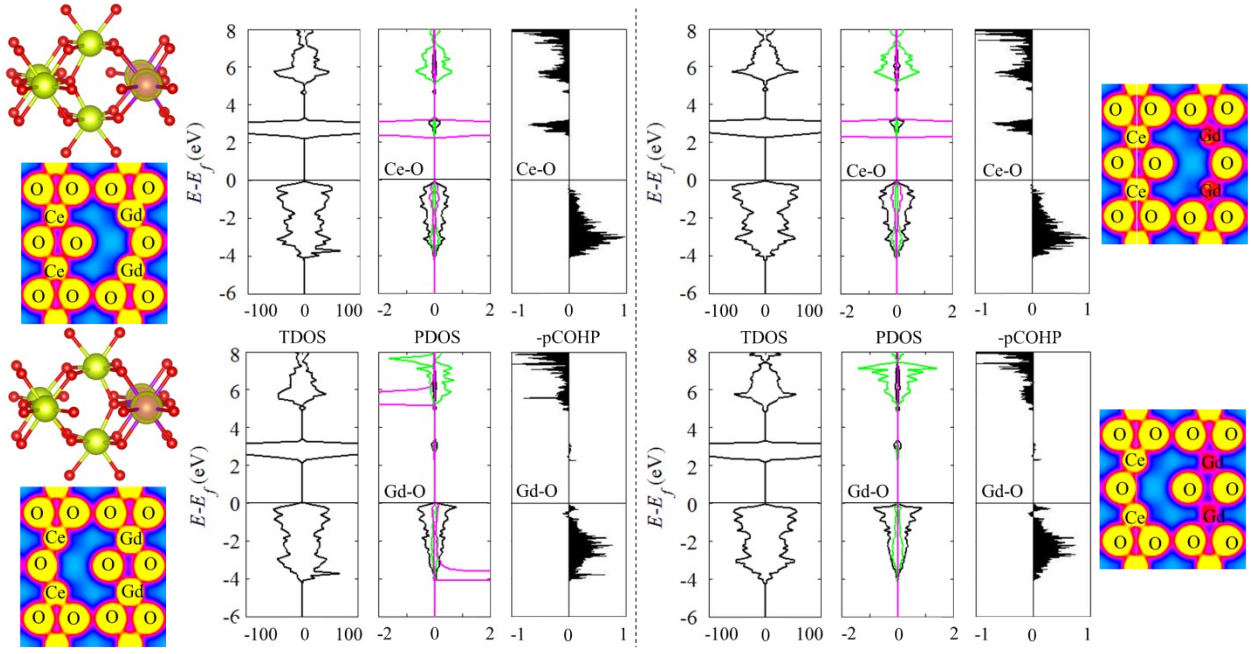

Figure S7. Charge density plots within energy range of O_{2p}-VB, total and projected DOS and the corresponding COHP curves of Gd-doped CeO_2 at initial and final states of ip1. Left panel shows the 4fval results while right panel shows the 4fcore results.

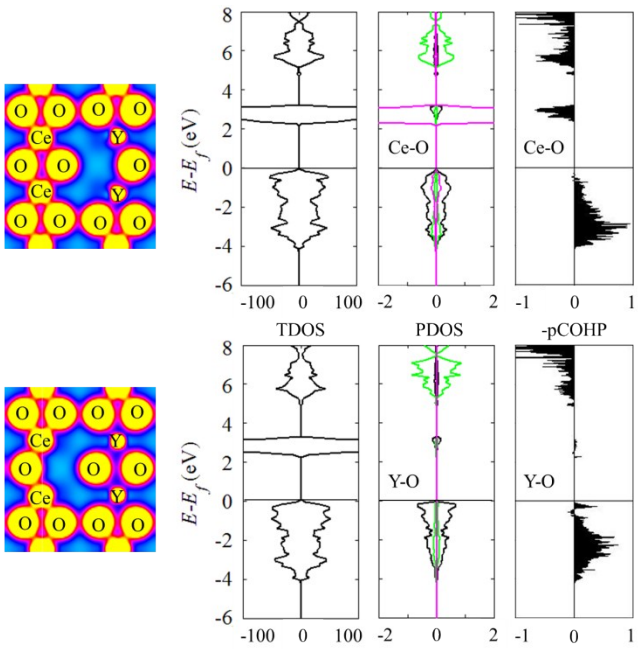

Figure S8. Charge density plots within energy range of O_{2p}-VB, total and projected DOS and the corresponding COHP curves of Y-doped CeO_2 at initial and final states of ip1.

[1] A. D. Becke, *The Journal of Chemical Physics*, 1993, 98, 1372-1377.