Supporting Information

A Systematic Evaluation of the Role of the Lanthanide Elements in Complex Functional Oxides; Implications for Energy Conversion Devices

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Table S1: Summary and comparison of experimental and calculated lattice parameters. For all the oxides investigated in this work, a = b. Errors are calculated with respect to the experimental values. Exp. stands for experimental lattice parameters.

Compound		*a (Å)*	*c (Å)*
La_2O_3	Exp. [1]	3.94	6.13
	LCAO PBE	3.99	6.27
	error	1.39%	2.21%
	LCAO PBE0	3.97	6.20
	error	0.74%	1.18%
	PAW PBE	3.92	6.17
	error	-0.53%	0.65%
	PAW PBE0	3.91	6.14
	error	-0.51%	0.16%
$LaAlO_3$	Exp. [2]	5.36382	13.1091
	LCAO PBE	5.434	13.234
	error	1.31%	0.95%
	LCAO PBE0	5.372	13.112
	error	0.15%	0.03%
	PAW PBE	5.379	13.017
	error	0.28%	-0.70%
	PAW PBE0	5.379	13.016
	error	0.28%	-0.71%
SrO	Exp. [3]	5.16132	5.16132
	LCAO PBE	5.127	5.127
	error	-0.67%	-0.67%
	LCAO PBE0	5.099	5.099
	error	-1.20%	-1.20%
	PAW PBE	5.127	5.127
	error	-0.67%	-0.67%
	PAW PBE0	5.127	5.127
	error	-0.67%	-0.67%
$SrTiO_3$	Exp. [4]	3.901	3.901
	LCAO PBE	3.924	3.924
	error	0.59%	0.5%
	LCAO PBE0	3.885	3.885
	error	-0.40%	-0.40%
	PAW PBE	3.923	3.923
	error	0.56%	0.56%
	PAW PBE0	3.921	3.921
	error	0.51%	0.51%
Pr_2O_3	Exp. [1]	3.8589	6.0131
	LCAO PBE	3.900	6.143
	error	1.07%	2.15%
	LCAO PBE0	3.898	6.113
	error	1.02%	1.67%

	PAW PBE	3.868	6.002
	error	0.25%	-0.19%
	PAW PBE0	3.814	5.971
	error	-1.15%	-0.69%
$PrAlO_3$	Exp. [5]	5.33313	12.9729
	LCAO PBE	5.415	13.138
	error	1.54%	1.27%
	LCAO PBE0	5.353	13.009
	error	0.38%	0.27%
	PAW PBE	5.333	12.972
	error	0.00%	0.00%
	PAW PBE0	5.365	12.982
	error	0.60%	0.07%
BaO	Exp. [6]	5.582	5.582
	LCAO PBE	5.498	5.498
	error	-1.50%	-1.50%
	LCAO PBE0	5.474	5.474
	error	-1.94%	-1.94%
	PAW PBE	5.614	5.614
	error	0.57%	0.57%
	PAW PBE0	5.614	5.614
	error	0.57%	0.57%
$BaTiO_3$	Exp. [7]	3.99095	4.0352
	LCAO PBE	3.996	4.124
	error	0.14%	2.21%
	LCAO PBE0	3.960	4.086
	error	-0.78%	1.25%
	PAW PBE	4.006	4.190
	error	0.37%	3.83%
	PAW PBE0	4.006	4.190
	error	0.37%	3.83%

Table S2: Comparison of the computed atomic charges of La and O in La-containing oxides. The atomic charges of La and O in the oxides were calculated using Mulliken population analysis and Bader charge analysis. The lattice structures were optimized before carrying out the charge analysis.

La Charge	O Charge	Compound	Theoretical Approximation	Charge Analysis Method	Reference	Basis Sets
2.359	-1.573	La_2O_3	Hartree-Fock	Mulliken	This work	LCAO
1.774	-1.183	La_2O_3	PBE	Mulliken	This work	LCAO
1.947	-1.298	La_2O_3	PBE0	Mulliken	This work	LCAO
2.428	-1.618	La_2O_3	Hartree-Fock	Bader	This work	PAW
2.001	-1.334	La_2O_3	PBE	Bader	This work	PAW
2.165	-1.444	La_2O_3	PBE0	Bader	This work	PAW
2.316	-1.471	$LaAlO_3$	Hartree-Fock	Mulliken	This work	LCAO
1.825	-1.201	$LaAlO_3$	PBE	Mulliken	This work	LCAO
1.944	-1.261	$LaAlO_3$	PBE0	Mulliken	This work	LCAO
2.498	-1.815	$LaAlO_3$	Hartree-Fock	Bader	This work	PAW
2.052	-1.689	$LaAlO_3$	PBE	Bader	This work	PAW
2.244	-1.748	$LaAlO_3$	PBE0	Bader	This work	PAW
2.043	-1.681	$LaAlO_3$	PW-91	Bader	[8]	PAW
2.076	-1.268	$LaMnO_3$	PW-91+U	Bader	[8]	PAW
2.09	-1.15	$La_{0.5}Sr_{0.5}Co_{0.25}Fe_{0.75}O_{3-\delta}$	PBE+U	Bader	[9]	PAW

Table S3: Comparison of the computed atomic charges of Sr and O in Sr-containing oxides. The atomic charges of Sr and O in the oxides were calculated using Mulliken population analysis and Bader charge analysis. The lattice structures were optimized before carrying out the charge analysis.

Sr Charge	O Charge	Compound	Theoretical Approximation	Charge Analysis Method	Reference	Basis Sets
1.848	-1.848	SrO	Hartree-Fock	Mulliken	This work	LCAO
1.734	-1.734	SrO	PBE	Mulliken	This work	LCAO
1.768	-1.768	SrO	PBE0	Mulliken	This work	LCAO
1.605	-1.605	SrO	Hartree-Fock	Bader	This work	PAW
1.424	-1.424	SrO	PBE	Bader	This work	PAW
1.475	-1.475	SrO	PBE0	Bader	This work	PAW
1.867	-1.580	$SrTiO_3$	Hartree-Fock	Mulliken	This work	LCAO
1.776	-1.384	$SrTiO_3$	PBE	Mulliken	This work	LCAO
1.804	-1.437	$SrTiO_3$	PBE0	Mulliken	This work	LCAO
1.871	-1.407	$SrTiO_3$	B3PW	Mulliken	[10]	LCAO
1.722	-1.707	$SrTiO_3$	Hartree-Fock	Bader	This work	PAW
1.593	-1.353	$SrTiO_3$	PBE	Bader	This work	PAW
1.631	-1.448	$SrTiO_3$	PBE0	Bader	This work	PAW
1.595	-1.266	$SrTiO_3$	PW-91	Bader	[8]	PAW

Table 4: Comparison of the computed atomic charges of Pr in Pr-containing oxides. The atomic charge of Pr in its oxides were calculated using Mulliken population analysis and Bader charge analysis. The lattice structures were optimized before carrying out the charge analysis.

Pr Charge	O Charge	Compound	Theoretical Approximation	Charge Analysis Method	Reference	Basis Sets
1.801	-1.262	Pr_2O_3	PBE	Mulliken	This work	LCAO
2.071	-1.381	Pr_2O_3	PBE0	Mulliken	This work	LCAO
1.963	-1.310	Pr_2O_3	PBE	Bader	This work	PAW
2.112	-1.408	Pr_2O_3	PBE0	Bader	This work	PAW
2.058	-1.301	$PrAlO_3$	PBE	Mulliken	This work	LCAO
2.194	-1.369	$PrAlO_3$	PBE0	Mulliken	This work	LCAO
2.021	-1.675	$PrAlO_3$	PBE	Bader	This work	PAW
2.201	-1.734	$PrAlO_3$	PBE0	Bader	This work	PAW

Table 5: Comparison of the computed atomic charges of Ba in Ba-containing oxides. The atomic charge of Ba in its oxides were calculated using Mulliken population analysis and Bader charge analysis. The lattice structures were optimized before carrying out the charge analysis.

Ba Charge	O Charge	Compound	Theoretical Approximation	Charge Analysis Method	Reference	Basis Sets
1.755	-1.755	BaO	PBE	Mulliken	This work	LCAO
1.790	-1.790	BaO	PBE0	Mulliken	This work	LCAO
1.436	-1.436	BaO	PBE	Bader	This work	PAW
1.496	-1.496	BaO	PBE0	Bader	This work	PAW
1.801	-1.391	$BaTiO_3$	PBE	Mulliken	This work	LCAO
1.826	-1.442	$BaTiO_3$	PBE0	Mulliken	This work	LCAO
1.541	-1.362	$BaTiO_3$	PBE	Bader	This work	PAW
1.603	-1.455	$BaTiO_3$	PBE0	Bader	This work	PAW
1.795	-1.386	$BaTiO_3$	B3PW	Mulliken	[10]	LCAO
1.58	-1.15	$Sm_{0.5}Ba_{0.5}CoO_{2.75}$	PBE+U	Bader	[11]	PAW

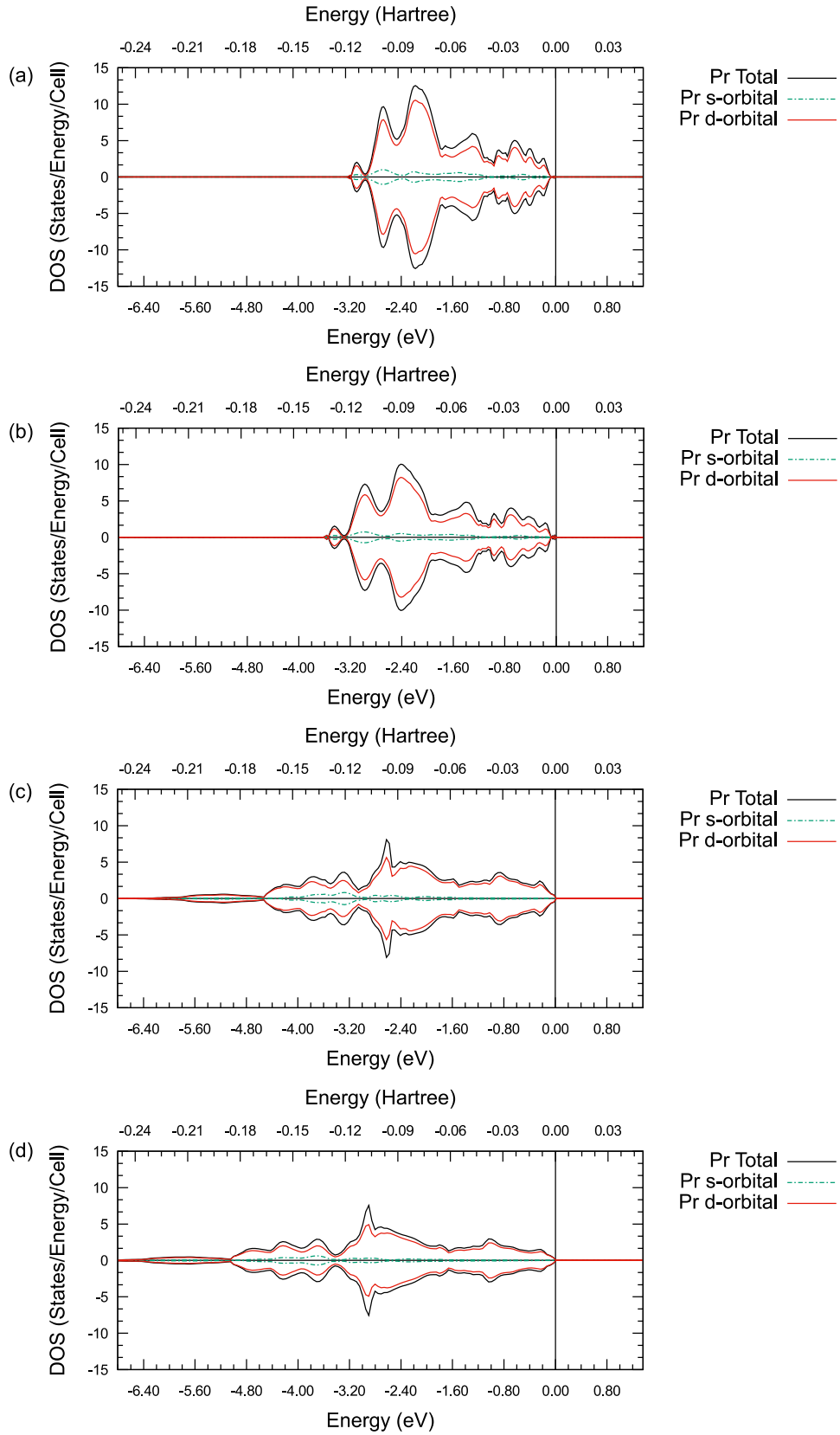

Figure S1: Projected Pr density of states for its s-orbitals and d-orbitals in Pr_2O_3 (3a and 3b) and $PrAlO_3$ (3c and 3d). 3a and 3c are calculated using the GGA-PBE functional. 3b and 3d are calculated using the hybrid PBE0 functional. The Fermi energy is marked as 0 eV on the energy scale in all plots.

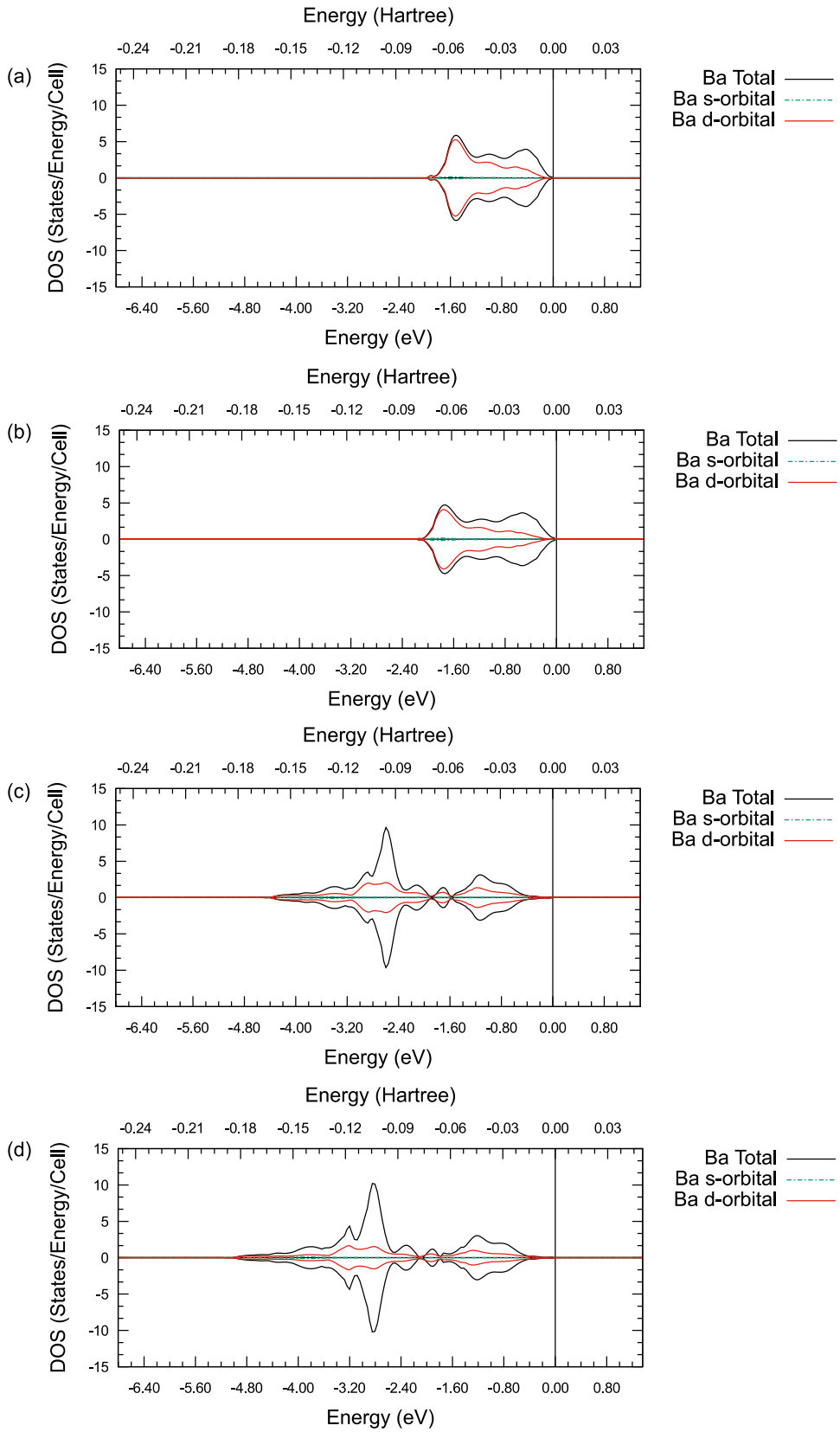

Figure S2: Projected Ba density of states for its s-orbitals and d-orbitals in BaO (4a and 4b) and $BaTiO_3$ (4c and 4d). 4a and 4c are calculated using the GGA-PBE functional. 4b and 4d are calculated using the hybrid PBE0 functional. The Fermi energy is marked as 0 eV on the energy scale in all plots.

References:

(1) Koehler, W. C.; Wollan, E. O. *Acta Crystallogr.* **1953**, *6* (8), 741.

(2) Lehnert, H.; Boysen, B.; Schneider, S. J.; Frey, F.; Hohlwein, D.; Radaelli, P.; Ehrenberg, H. *Zeitschrift für Krist.* **2000**, *215* (9), 536.

(3) Bashir, J.; Khan, R. T. A.; Butt, N. M.; Heger, G. *Powder Diffr.* **2002**, *17* (3), 222.

(4) Abramov, Y. A.; Tsirelson, V. G.; Zavodnik, V. E.; Ivanov, S. A.; Brown, I. D. *Acta Cryst.* **1995**, *B51*, 942.

(5) Zhao, J.; Ross, N. L.; Angel, R. J.; Carpenter, M. a; Howard, C. J.; Pawlak, D. a; Lukasiewicz, T. *J. Phys. Condens. Matter* **2009**, *21* (23), 235403.

(6) Ghebouli, M. A.; Ghebouli, B.; Bouhemadou, A.; Fatmi, M.; Bouamama, K. *J. Alloys Compd.* **2011**, *509* (5), 1440.

(7) Kwei, G. H.; Lawson, a C.; Billinge, S. J. L.; Cheong, S. W. *J. Phys. Chem.* **1993**, *97*, 2368.

(8) Lee, Y.-L.; Morgan, D. *Phys. Rev. B* **2015**, *91* (19), 195430.

(9) Ritzmann, A. M.; Dieterich, J. M.; Carter, E. A. *Phys. Chem. Chem. Phys.* **2016**, *18*, 12260.

(10) Piskunov, S.; Heifets, E.; Eglitis, R. I.; Borstel, G. *Comput. Mater. Sci.* **2004**, *29* (2), 165.

(11) Olsson, E.; Aparicio-Anglès, X.; de Leeuw, N. H. *Phys. Chem. Chem. Phys.* **2017**, *19* (21), 13960.