Supplementary Information for

Sulfur-doping effects on the oxygen vacancy formation of $LaBO_3$ (B= Fe, Co, and Ni) perovskites

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Defect formation energy

The defect formation energy of one S substitution for O in our 2 × 2 × 2 $LaBO_3$ supercells can be described by

$$E_f(F_O) = 8E_{tot}(LaBO_{2.875}S_{0.125}) - 8E_{tot}(LaBO_3) + \mu_O - \mu_S.$$

The $E_{tot}(LaBO_{2.875}S_{0.125})$ and $8E_{tot}(LaBO_3)$ are the total energy of defect $LaBO_{2.875}S_{0.125}$ and pristine $LaBO_3$ systems, while μ_O and μ_S are the chemical potential of oxygen and sulfur atoms. Therefore, the $E_f(F_O)$ depends on the two independent variables of μ_O and μ_S.

The O-rich and S-rich limit of $\mu_O(rich)$ and $\mu_S(rich)$ were calculated from the corresponding elemental solid of O_2 and S_8 molecules, resulting in the values of -4.247 eV and -4.126 eV, respectively. On the opposite, we considered the formation of $La_2B_2O_5$ in the extreme O-poor condition, and the condition of equilibrium between LaS_2 and LaS in the extreme S-poor condition, where the $\mu_S(poor)$and $\mu_O(poor)$ were estimated from

$$\mu_S = E_{tot}(LaS_2) - E_{tot}(LaS) = -5.405\ eV,$$

$$\mu_O = 2E_{tot}(LaBO_3) - E_{tot}(La_2B_2O_5).$$

The $\mu_O(poor)$ for $LaBO_3$ were shown in Tables S1, with the correspond defect formation energy $E_f(F_O)$ at O-poor/S-rich and O-rich/S-poor cases. The values of $E_f(F_O)$ at O-poor/S-rich case are

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lower than O-rich/S-poor cases. It is reasonable that S substitution for O is easier at O-poor/S-rich conditions.

Table S1: The total energies (eV/f.u.) of related compounds, and the calculated $\mu_O(poor)$ and defect formation energy $E_f(F_O)$ at O-poor/S-rich and O-rich/S-poor cases for $LaBO_3$.

B	$LaBO_{2.875}S_{0.125}$	$LaBO_3$	$La_2B_2O_5$	$\mu_O(poor)$ (eV)	$E_f(F_O)$ (O-poor/S-rich, eV)	$E_f(F_O)$ (O-rich/S-poor, eV)
Fe	-37.693	-38.276	-68.716	-7.837	0.900	5.821
Co	-35.179	-35.647	-65.433	-5.860	1.980	4.873
Ni	-32.964	-33.490	-61.024	-5.957	2.380	5.371

Table S2. The distances of B-O and O-B in B-O-B chains to create V_O, and the formation energies E_f (eV), related electrostatic E_{bond} (eV) and structural relaxation E_{relax} (eV) terms for $LaBO_{3-\delta}$.

B	*Distances of B-O , O-B (Å)*	E_f (eV)	E_{bond} (eV)	E_{relax} (eV)
Fe	2.042, 2.029	4.227	4.707	-0.480
	2.031, 2.031	4.232	4.755	-0.523
Co-LS	1.943, 1.943	3.324	4.140	-0.816
Co-HS	2.084, 1.926	2.463	3.127	-0.664
	2.056, 2.054	2.261	3.495	-1.234
Co-IS	1.959, 1.959	1.822	3.122	-1.300
	1.999, 1.999	1.883	2.910	-1.027
Ni	1.956, 1.955	1.539	2.643	-1.104

Table S3. The octahedra, the distances of B-O and O-B in B-O-B chains to create V_O, and the formation energies E_f (eV), related electrostatic E_{bond} (eV) and structural relaxation E_{relax} (eV) terms for $LaFeO_{2.875-\delta}S_{0.125}$.

Octahedra	*Distances of Fe-O, O-Fe (Å)*	E_f (eV)	E_{bond} (eV)	E_{relax} (eV)
$Fe1O_5S$	2.026, 2.089	3.282	4.330	-1.048
	2.055, 2.061	3.741	4.472	-0.731
	1.919, 1.924	3.856	4.389	-0.633
$Fe2O_6$	2.084, 2.106	3.813	4.745	-0.932
	2.032, 2.041	4.051	4.669	-0.618
$Fe3O_6$	2.075, 2.088	4.201	4.755	-0.554
	2.045, 2.051	4.253	4.731	-0.478

Table S4. The octahedra, the distances of B-O and O-B in B-O-B chains to create V_O, and the formation energies E_f (eV), related electrostatic E_{bond} (eV) and structural relaxation E_{relax} (eV) terms for LS $LaCoO_{2.875-\delta}S_{0.125}$.

Octahedra	*Distances of Co-O, O-Co (Å)*	E_f (eV)	E_{bond} (eV)	E_{relax} (eV)
$Co1O_5S$	1.981, 1.981	2.515	3.769	-1.254
	1.941, 1.995	2.398	4.023	-1.625
	1.878, 1.879	2.755	3.722	-0.968
$Co2O_6$	1.990, 1.991	2.905	4.034	-1.129
	1.959, 1.960	3.036	3.995	-0.959
$Co3O_6$	1.990, 1.991	3.366	4.336	-0.970
	1.935, 1.936	3.589	3.920	-0.531

Table S5. The octahedra, the distances of B-O and O-B in B-O-B chains to create V_O, and the formation energies E_f (eV), related electrostatic E_{bond} (eV) and structural relaxation E_{relax} (eV) terms for HS $LaCoO_{2.875-\delta}S_{0.125}$.

Octahedra	*Distances of Co-O, O-Co (Å)*	E_f (eV)	E_{bond} (eV)	E_{relax} (eV)
$Co1O_5S$	1.972, 2.059	1.964	3.224	-1.260
	1.889, 2.170	1.607	3.058	-1.451
	1.922, 1.937	1.761	3.756	-1.995
$Co2O_6$	2.078, 2.085	1.918	3.354	-1.436
	1.884, 2.107	1.993	3.205	-1.212
$Co3O_6$	2.101, 2.107	2.165	3.490	-1.325
	2.036, 2.044	2.211	3.238	-1.027

Table S6. The octahedra, the distances of B-O and O-B in B-O-B chains to create V_O, and the formation energies E_f (eV), related electrostatic E_{bond} (eV) and structural relaxation E_{relax} (eV) terms for IS $LaCoO_{2.875-\delta}S_{0.125}$.

Octahedra	*Distances of Co-O, O-Co (Å)*	E_f (eV)	E_{bond} (eV)	E_{relax} (eV)
$Co1O_5S$	2.046, 1.957	1.823	3.191	-1.368
	2.010, 1.943	1.583	2.936	-1.353
	1.928, 1.929	1.885	3.019	-1.134
$Co2O_6$	2.024, 2.022	2.097	3.567	-1.470
	2.006, 1.920	2.138	3.655	-1.517
$Co3O_6$	2.055, 2.042	2.679	3.629	-0.950
	1.996, 1.985	2.348	3.157	-0.809

Table S7. The octahedra, the distances of B-O and O-B in B-O-B chains to create V_O, and the formation energies E_f (eV), related electrostatic E_{bond} (eV) and structural relaxation E_{relax} (eV) terms for $LaNiO_{2.875-\delta}S_{0.125}$.

Octahedra	*Distances of Ni-O, O-Ni (Å)*	E_f (eV)	E_{bond} (eV)	E_{relax} (eV)
$Ni1O_5S$	1.951, 2.046	0.939	2.299	-1.360
	1.932, 2.002	0.826	2.200	-1.374
	1.876, 1.876	1.011	2.151	-1.140
$Ni2O_6$	1.980, 1.991	1.269	2.739	-1.470
	1.964, 1.979	1.479	2.764	-1.285
$Ni3O_6$	1.998, 1.998	1.835	3.071	-1.236
	1.949, 1.948	1.577	2.700	-1.123