Supporting Information for:

Generalized Trends in the Formation Energies of Perovskite Oxides

ZhenHua Zeng[1], Federico Calle-Vallejo[2], Mogens B. Mogensen[3] and Jan Rossmeisl[1]
[1]*Center for Atomic-Scale Materials Design, Department of Physics, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark*
[2]*Leiden Institute of Chemistry, Leiden University, PO box 9502, 2300 RA Leiden, The Netherlands*[3]*Department of Energy Conversion and Storage, DTU Risø Campus, Technical University of Denmark, P.O. Box 49, 4000 Roskilde, Denmark*

1. Correlation between Formation Energies of Sesquioxides and Perovskites

Fig. S1 contains a similar analysis to that of Fig. 6 in the main text. In this case, the data are for sesquioxides and perovskites with rare-earth metals (namely Y and La) at the A site. As previously observed for the other families of perovskites, the slopes of the lines are unitary and the offsets are negative.

According to the experimental data in Fig. S.1 (an equivalent analysis can be made with the DFT data), the following relationship holds if the A site is either occupied by Y or La and the B site is occupied by a transition metal:

$$\Delta G_{ABO_3} - 1/2\,\Delta G_{B_2O_3} \approx -9.35 \qquad (1)$$

The consequence of this observation is that ABO_3 and B_2O_3 are analogous compounds energetically-speaking. The traditional method to prepare this kind of ABO_3 oxides is the combination of the sesquioxides A and B components (A_2O_3 and B_2O_3, respectively), as shown in Eq(2):

$$1/2\,A_2O_{3(s)} + 1/2\,B_2O_{3(s)} \rightarrow ABO_{3(s)} \qquad (2)$$

The free energy of Eq(2) is given below:

$$\Delta G_2 = \Delta G_{ABO_3} - 1/2\,\Delta G_{B_2O_3} - 1/2\,\Delta G_{A_2O_3} \approx -\left(9.35 + 1/2\,\Delta G_{A_2O_3}\right) \qquad (3)$$

Combining this result with the experimental formation energies of La2O3 (-17.70 eV), and Y2O3 (-18.79 eV),[1, 2] we conclude that the free energy of Reaction (3) is, to a first approximation, independent of the nature of the B component and depends mostly on the formation energies of the sesquioxides of the A component. Thus, the free energy of Eq(2) is approximately -0.50 eV for $LaBO_3$, in good agreement with the average value in Ref. 1 of -0.43 eV. The approximately constant reaction energy of Eq(2) implies again, as for the case of Ca-, Sr-, and Ba-perovskites, that the contributions of the elements at the A and B sites to the energetics of ABO_3 are different and easily disentangled, as they are only a linear superposition of the effects of both components.

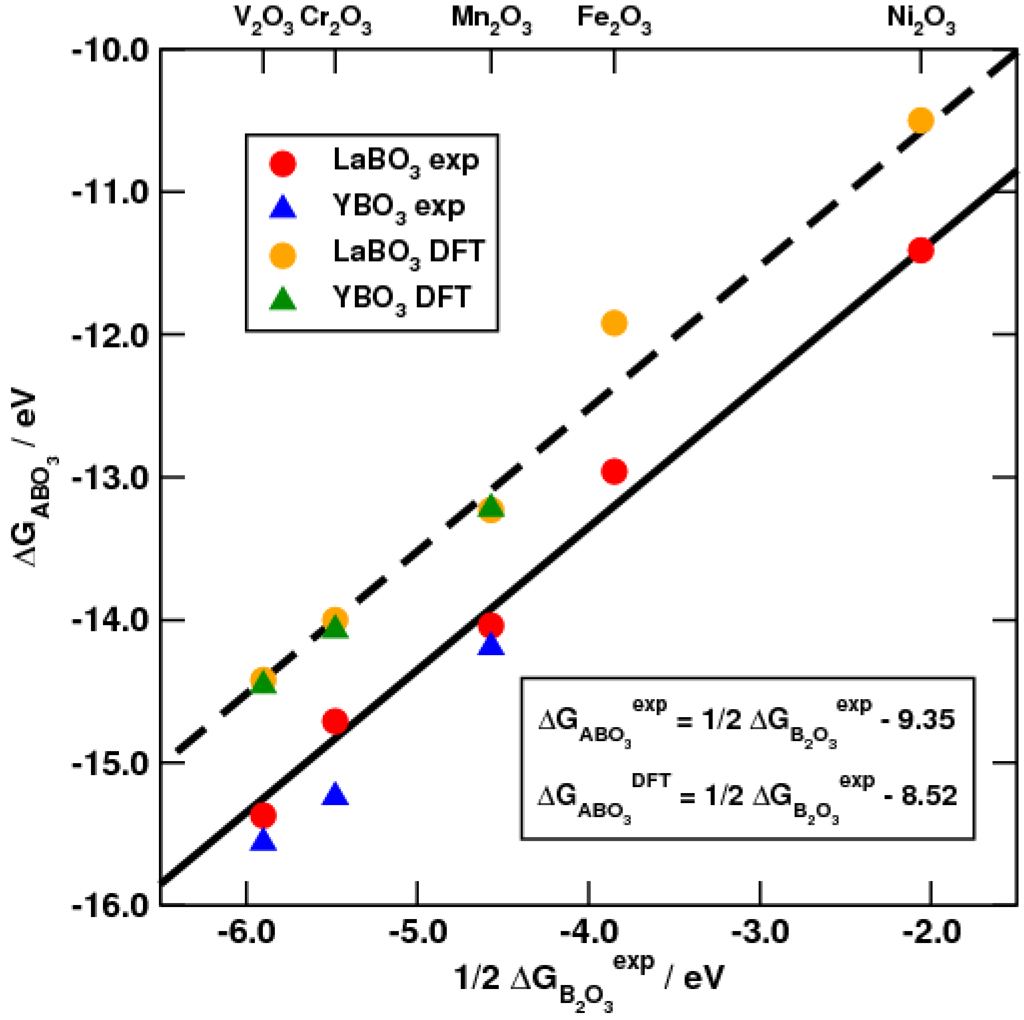

Figure S1. Relation between the formation energies of ABO_3 (both calculated and experimental data, see Ref. 1 and references therein) and $0.5B_2O_3$(experimental data from Refs.2, 3), for the rare-earth metals Y and La at the A site, and 3*d* transition metals V, Cr, Mn, Fe and Ni at the B site, respectively. The unitary slope and the negative offset have deep implications on the thermochemistry of these compounds; see the main text for further information.

2. Formation Energies of Selected Oxides

In Table S1 we present the calculated and experimental data for AO (with A = Ca, Sr, Ba) and various Ti oxides.

Table S1. Calculated and experimental free energies of formation of AO (with A = Ca, Sr, Ba), TiO_2 and $ATiO_3$ at 298 K. Experimental data are taken from Ref. 2.

Oxide	ΔG^{DFT} / eV	ΔG^{exp} / eV
CaO	-5.55	-6.28
SrO	-5.16	-5.82
BaO	-4.80	-5.36
TiO_2	-8.81	-9.25
$CaTiO_3$	-15.07	-16.33
$SrTiO_3$	-15.12	-16.46
$BaTiO_3$	-14.88	-16.40

The DFT-calculated formation energies of BO_3 and ABO_3 with Na at the A site and 3d metals from Ti to Cu at the B site can be found in Table S2.

Table S2. Calculated Gibbs free energies of formation of various 3d perovskites at 298 K.

3d Oxide	ΔG / eV
TiO_3	-6.42
VO_3	-5.02
CrO_3	-4.03
MnO_3	-2.64
FeO_3	-0.51
CoO_3	1.01
NiO_3	2.28
CuO_3	3.76
$NaTiO_3$	-10.84
$NaVO_3$	-9.06
$NaCrO_3$	-7.57
$NaMnO_3$	-6.16
$NaFeO_3$	-4.29
$NaCoO_3$	-3.11
$NaNiO_3$	-2.18
$NaCuO_3$	-1.05

The DFT-calculated formation energies of BO_3 and ABO_3 with vacancies, Na, K, Ca, Sr and Y at the A site and 5d metals from Ta to Pt at the B site can be found in Table S3.

Table S3. Calculated Gibbs free energies of formation of various 5d perovskites at 298 K.

5d oxide	ΔG / eV
TaO_3	-8.05
WO_3	-7.06
ReO_3	-5.70
OsO_3	-2.92
IrO_3	-0.76
PtO_3	1.41
$NaTaO_3$	-12.07
$NaWO_3$	-9.22
$NaReO_3$	-7.51
$NaOsO_3$	-5.17
$NaIrO_3$	-3.66
$NaPtO_3$	-2.32
$KTaO_3$	-12.06
KWO_3	-9.18
$KReO_3$	-7.36
$KOsO_3$	-5.07
$KIrO_3$	-3.58
$KPtO_3$	-2.25
$CaTaO_3$	-12.88
$CaWO_3$	-10.21
$CaReO_3$	-8.95
$CaOsO_3$	-7.67
$CaIrO_3$	-7.45
$CaPtO_3$	-5.93
$SrTaO_3$	-13.17
$SrWO_3$	-10.44
$SrReO_3$	-9.00
$SrOsO_3$	-7.34
$SrIrO_3$	-7.21
$SrPtO_3$	-6.05
$YTaO_3$	-13.25
YWO_3	-11.53
$YReO_3$	-10.07
$YOsO_3$	-9.19
$YIrO_3$	-8.71
$YPtO_3$	-8.45

In Table S4 we present the calculated and experimental free energies of Reaction (4) in the main text ($AO_{(s)} + BO_{2(s)} \rightarrow ABO_{3(s)}$), adapted from Ref. 1 and references therein. The average reaction energies from calculations/experiments are -0.69/-0.83 eV for $CaBO_3$, -1.02/-1.18 eV for $SrBO_3$ and -1.56/-1.58 eV for $BaBO_3$. These numbers are in good agreement with the values predicted in the present work: -0.82 eV, -1.25 eV, and -1.68 eV.

Table S4. Calculated and experimental free energies of formation of $ATiO_3$ from AO (with A = Ca, Sr, Ba), TiO_2 at 298 K. Experimental data are taken from the Supporting Information of Ref. 1 and references therein.

Perovskite	ΔG_{DFT} / eV	ΔG_{EXP} / eV
$CaTiO_3$	-0.87	-0.84
$CaCrO_3$	-0.48	-0.73
$CaMnO_3$	-0.72	-0.91
$SrTiO_3$	-1.19	-1.24
$SrVO_3$	-1.34	-1.46
$SrCrO_3$	-0.69	-1.09
$SrMnO_3$	-0.85	-0.92
$BaTiO_3$	-1.56	-1.58

3. Comparison between RPBE, PBE and hybrid functionals

The choice of RPBE in combination with H_2O and H_2 references instead of using O_2 directly is made to avoid the large error in the formation energy introduced by the remarkably poor description of the triplet state of O_2 in standard DFT calculations, which results in a wrong description of the energetics of this molecule. In order to quantify this statement, consider the atomization energies of O_2 ($O_2 \rightarrow 2O$) in the second column of Table S5. The energies are from two GGAs,[4] i.e. PBE and RPBE, and three hybrid functionals, i.e. B3LYP,[5] PBE0[6] and HSE06[7, 8]. According to the values in Table S5, the error in calculating the atomization energy of O_2 is 1.01 eV for PBE and 0.56 eV for RPBE, respectively. The error is much smaller for hybrid functionals, especially for HSE06. Note that these functionals are, computationally speaking, rather expensive, especially for calculations of extended systems. On the other hand, the description of O, H, H_2 and H_2O is much better in standard DFT calculations. For example, the error in calculating the atomization energy of H_2 ($H_2 \rightarrow 2H$) and H_2O ($H_2O \rightarrow 2H+O$) are around

0.20 eV for both PBE and RPBE. In fact, the deviations for hybrid functionals are also in this range.

Now consider the reaction: $H_2O \rightarrow H_2 + O$. The reaction energy can be written as:

$$\Delta E\left(H_2O \rightarrow H_2 + O\right) = E_t\left(\mathrm{H_2}\right) + E_t\left(\mathrm{O}\right) - E_t\left(\mathrm{H_2O}\right) = E_A\left(\mathrm{H_2O}\right) - E_A\left(\mathrm{H_2}\right) \qquad (4)$$

Where E_t and E_A are the total and the atomization energies of the species. The reaction energies from experiments and DFT calculations with various functionals are given in Table S5, along with the difference with respect to the experimental value of 5.32 eV. Note that the reaction energy for RPBE (5.25 eV) is very close to the experimental value. This deviation, i.e. 0.07 eV, is also much smaller than the typical error in H_2 or H_2O alone, i.e. around 0.2 eV. The corresponding deviations for hybrid functionals oscillate between 0 and 0.03 eV, and 0.3 eV for PBE, respectively. Therefore, the description of this reaction within the RPBE formalism is remarkably accurate and close to the more sophisticated hybrid functionals. The implication of this is that using H_2 and H_2O references, or alternatively the O reference in RPBE, can significantly minimize the error in the formation energy introduced by the inaccurate description of O_2. In the present study we use the former approach: the energetics of O_2 is calculated indirectly in the following way: $E_{O_2}^{DFT} = 2(E_{H_2O}^{DFT} - E_{H_2}^{DFT} + \Delta ZPE - T\Delta S - \Delta G_w)$ with $\Delta G_w = -2.37\ eV$ the formation energy of H_2O (g) at standard conditions. We note that using the O reference would essentially give identical accuracy, as Eq. 4 can be rewritten as $E_t(H_2O) - E_t(H_2) = E_t(O) - \Delta E$.

Moreover, Martinez et al found that this scheme (RPBE in combination with H_2O and H_2 as gas-phase references) performs quite well in its description of the formation energies of rutile oxides, while PBE has a systematic error of approximately -0.8 eV. This similarity between experiments and DFT calculations has been attributed to the improved description of exchange achieved by RPBE with respect to PBE.[9]

Table S5. Experimental and DFT-calculated energetics (in eV) of O_2, H_2 and H_2O. Zero-point vibration has been removed from experimental data.

	$E_A(O_2)$	$E_A(H_2)$	$E_A(H_2O)$	$\Delta E(H_2O \rightarrow H_2+O)$	ΔE^{DFT}-ΔE^{exp}
Exp.[a]	5.22	4.75	10.07	-5.32	--
PBE[a]	6.23	4.54	10.16	-5.62	-0.30
RPBE[a]	5.78	4.57	9.83	-5.25	0.07
B3LYP[b]	5.44	4.68	9.97	-5.29	0.03
PBE0[c]	5.36	4.57	9.87	-5.30	0.02
HSE06[d]	5.24	4.53	9.85	-5.32	0.00

[a] Ref. 4,

[b] Ref. 5

[c] Ref. 6

[d] Ref. 7, 8.

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