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

Is ReO_3 a mixed ionic–electronic conductor? A DFT study of defect formation and migration in a $B^{VI}O_3$ perovskite-type oxide

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Supplementary Material

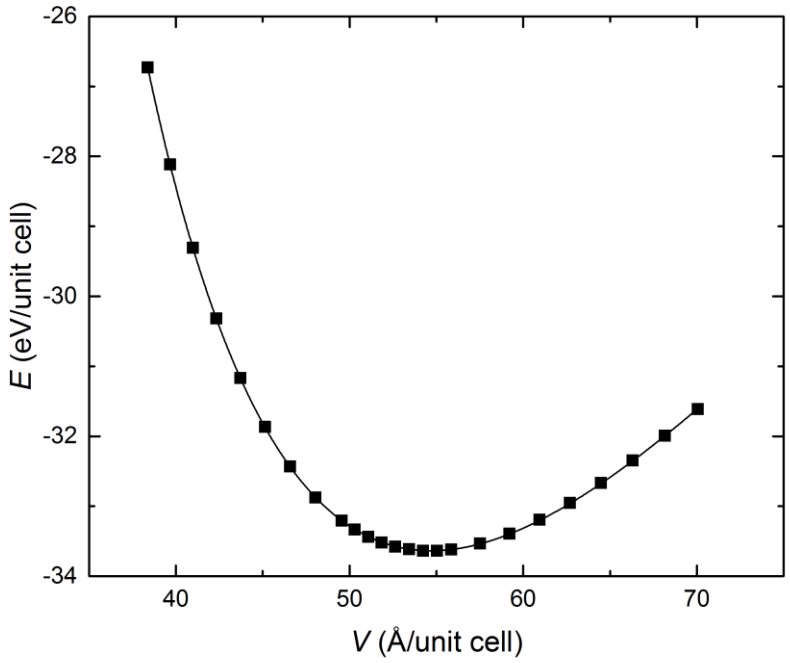

Fig. S1: Energy-volume curve of ReO_3. The calculated values are fitted with the Birch–Murnaghan equation.[1,2]

Table S1 Angles and distances of H_3O^+ in ReO_3 occupying an *A* site in comparison to the values of H_3O^+ in different crystals.

	d_{O-H} (Å)	H–O–H angle	d_{H-H} (Å)	Ref.
H_3O^+ in ReO_3	1.015	106°–111°	1.62–1.68	This work
H_3O^+ in $HCl{\cdot}H_2O$	0.96±0.08	~117°	1.65	[3]
H_3O^+ in $HNO_3{\cdot}H_2O$	~1.02		1.72±0.02	[4]
H_3O^+ in $HNO_3{\cdot}H_2O$	0.88–0.96	105.2°–115.6°		[5]

Table S2 Migration energy of oxide ions $\Delta E_{\mathrm{mig}}^{\mathrm{O}}$ in ReO_3 in comparison to the oxide-ion migration energies of perovskites. The path curvature is the distance between the oxide ion at the saddle point from the linear path.

	Method	$\Delta E_{\mathrm{mig}}^{\mathrm{O}}$ (eV)	Path curvature (Å)	Ref.
ReO_3	DFT	0.51	0.24	This work
$ReO_3 + Na_A^{\bullet}$	DFT	0.39	0.22	This work
$SrTiO_3$	DFT	0.53/0.46		6,7
$SrTiO_3 + v_{Sr}''$	DFT	0.89		6
$SrTiO_3$	exp.	0.62–0.67		8–13
$SrZrO_3$	atomistic simulations	0.58	0.2	14
$SrZrO_3$	exp.	0.47		15
$CaZrO_3$	atomistic simulations	0.42	0.42	14
$CaZrO_3$	exp.	1.8–2.6		16–20
$CaTiO_3$	exp.	0.56–3.99		21–23
$BaZrO_3$	DFT	0.69		7
$BaZrO_3$	exp.	≈ 1		24–28
$BaCe_{0.9}Y_{0.1}O_{2.95}$	exp.	0.62		24,29,30
$BaTiO_3$	DFT	0.67		7
$BaTiO_3$	exp.	0.7		31
$Pb(Zr,Ti)O_3$	exp.	0.56–0.91		32–34
$LaCrO_3$	interatomic pot. calc.	0.48	0.42	35
$LaMnO_3$	interatomic pot. calc.	0.86	0.43	35
$LaFeO_3$	interatomic pot. calc.	0.50	0.43	35
$LaCoO_3$	interatomic pot. calc.	0.61	0.25	35
$LaGaO_3$	exp.	0.6–1.0		36–40,40

Table S3 Activation energy of proton migration, $\Delta E_{\mathrm{mig}}^{\mathrm{H}}$ in ReO_3 in comparison with values for other perovskites. The *intra*octahedral migration is mentioned as well as the *inter*octahedral migration and the reorientation.

	Method	$\Delta E_{\mathrm{mig,intraoct.}}^{\mathrm{H}}$ (eV)	$\Delta E_{\mathrm{mig,interoct.}}^{\mathrm{H}}$ (eV)	$\Delta E_{\mathrm{reor}}^{\mathrm{H}}$ (eV)	Ref.
ReO_3	DFT	0.57	0.74	0.05	This work
$CaZrO_3$	DFT	0.58/0.74	0.14		41
$BaZrO_3$	DFT	0.21		0.18	42
	DFT	0.69			43
	DFT	0.83 ± 0.65			44
In-doped $BaZrO_3$	DFT	0.37			45
$BaZrO_3$	DFT	0.25		0.14	46

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