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## **Supplementary Information for RSC Advances**

## Discovery of zirconium dioxides for the design of better oxygen-ion conductors

## using efficient algorithms beyond data mining

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Space group	Oxide reported in	Index
type	Materials Project	
	Database	
Ama2	SiO <sub>2</sub>	Too large displacement after atomic relaxation of supercell with a $V_0$
$C222_{1}$	$SiO_2$	Too large displacement after atomic relaxation of supercell with a $V_0$
Cmce	$SiO_2$	Difficulty in convergence for structural optimization
Fd-3m	TiO <sub>2</sub>	Too large displacement after atomic relaxation of supercell with a $V_{\rm O}$
I-42d	$SiO_2$	Difficulty of convergence for structural optimization
Ima2	$SiO_2$	Too large displacement after atomic relaxation of supercell with a $V_0$
$P2_1$	$SiO_2$	Too large displacement after atomic relaxation of supercell with a $V_0$
$P3_{1}21$	TiO <sub>2</sub>	Too large displacement after atomic relaxation of supercell with a $V_0$
$P6_{2}22$	$SiO_2$	Difficulty of convergence for structural optimization
$P6_{3}22$	$SiO_2$	Too large displacement after atomic relaxation of supercell with a $V_0$
$P6_{4}22$	$SiO_2$	Too large displacement after atomic relaxation of supercell with a $V_{\rm O}$
$P6_{5}22$	$SiO_2$	Too large displacement after atomic relaxation of supercell with a $V_{\rm O}$
Pnnm	$SiO_2$	Difficulty in convergence for structural optimization

Table S1 List of excluded crystal structures which were reoptimized for  $ZrO_2$ .



**Fig. S1** Comparison of (a)  $E_g$  and (b)  $E_v$  obtained by the GGA and GGA+U methods of the 16 crystal structures of *reoptimized-ZrO*<sub>2</sub>. The  $E_g^{GGA+U}$  are all larger than the  $E_g^{GGA}$ , whereas the  $E_v$  from the GGA+U are slightly larger or similar as the  $E_v$  from the GGA. Diagonal line denotes that the values of the GGA and GGA+U become the same.

 Table S2 Chemical potential of O for the O-rich condition.

	Energy (eV/atom)	Index
From energy of O atom	-1.57	
From energy of $O_2$ gas molecule	-4.93	Used in this study.
From energy of $O_2$ gas molecule which is corrected	-4.25	From [Wang et al., Phys. Rev.
by comparison of formation energy of various oxides		B 2006, <b>73</b> , 195107].
between the theory and experiment		

Space group	$E_{\alpha}^{\text{GGA+U}}$	Averaged $E_{\rm m}(V_{\rm O}^0)$	$E_{\rm w}(V_{\rm O}^{0})$	$E_{\rm v}$ ( $V_{\rm O}^{2+}$ ) at the	Thermodynamic
Space Broap	Ξg	11, <b>et age a</b> 27 († 0 )	27(70)	center of $E_{\alpha}$	transition level $\varepsilon(2+/0)^{a}$
$P2_{1}/c$	3.53	6.15	6.16	4.52	2.59
-			6.13	5.32	2.17
Pbca	3.52	6.15	6.14	4.50	2.58
			6.15	5.43	2.13
$I4_1/amd$	3.89	6.40	6.40	5.03	2.63
$P2_1/m$	3.85	6.40	6.41	5.35	2.46
			6.38	4.98	2.62
C2/c	3.85	6.38	6.38	4.89	2.67
$Pca2_1$	3.78	5.93	5.93	5.02	2.35
			5.93	4.80	2.46
$P4_{1}2_{1}2$	3.51	6.71	6.71	5.54	2.35
$P4_2/mnm$	3.55	6.68	6.68	5.56	2.34
Pnma	4.11	6.06		NA <sup>b</sup>	NA <sup>b</sup>
$P4_2/nmc$	3.89	5.81	5.81	3.41	3.14
Pbcn	3.85	5.82	5.82	3.62	3.03
Fm-3m	3.38	5.84	5.84	3.63	2.85
P4/n	3.34	5.71	5.80	3.15	3.00
			5.35	3.42	2.64
			5.71	4.12	2.47
			5.67	3.96	2.53
$Pna2_1$	2.80	5.14	5.30	3.48	2.31
			4.97	3.64	2.07
<i>R</i> -3	3.75	5.93	5.87	4.07	2.78
			6.00	4.20	2.78
$P6_3mc$	3.75	6.51		NA <sup>b</sup>	NA <sup>b</sup>

**Table S3** Computed  $E_{\nu}$  for the 16 crystal structures of *reoptimized-ZrO*<sub>2</sub>. Abbreviation of VBM indicates the valence band maximum. All the values are in eV.

<sup>a</sup> If the image charge correction for the charged  $V_0$  are performed, the location of transition levels may become deeper because the  $E_v$  for the  $V_0^{2^+}$  at the VBM are mostly underestimated without the correction [Kumagai *et al.*, Phys. Rev. B 2014, **89**, 195205]. However, the correction may not affect the fact that the transition levels of  $\varepsilon(2+/0)$  are deep; it is known that the  $E_v(V_0^{2^+})$  in the *Fm*-3*m* structure of ZrO<sub>2</sub> can be corrected with ~0.25 eV increased value when the dielectric constant of ~37 is used [Liu *et al.*, Comput. Mater. Sci. 2014, **92**, 22].

<sup>b</sup> Not applicable.



**Fig. S2** (a) Three types of migration paths for the  $V_0$  to migrate to the nearest-neighboring O sites are considered with the cutoff radius of 3.5 Å. As an example,  $P4_2/nmc$  structure of  $ZrO_2$  is shown. Relative energies of the intermediates images (states) for a migration of  $V_0$  on the (b) path A < 110>, (c) path B < 001>, and (d) path *C*. Among three types of the migration paths, the lowest  $E_m$  of this structure is 0.34 eV on the path *A*.



**Fig. S3** Pattern of energy diagram for the minimum barrier energy for a  $V_0$  to migrate into the original site in the nearest-neighboring supercell from the examples of the (a) Fm-3m, (b)  $Pna2_1$ , (c)  $P2_1/c$ , (d) R-3, and (e) P4/n structures of ZrO<sub>2</sub>. In cases of (a)–(c), a  $V_0$  can migrate into the original site in the nearest neighboring supercell with only one type of migration. In cases of (d) and (e), a  $V_0$  should migrate into the original site in the nearest-neighboring supercell with different types of migrations. The numerical values are in eV.

Pattern	<pre># of types of O sites</pre>	Crystal structures	Description <sup>a</sup>
Pattern	1	$I4_1/amd, C2/c, P4_12_12,$	The $V_{\rm O}$ at an O-I site can hop between the O-I sites with one kind
(a)		$P4_2/mnm$ , $P4_2/nmc$ ,	of barrier energy.
		Pbcn, Fm-3m	$(0-I \rightarrow 0-I \rightarrow 0-I \rightarrow 0-I \rightarrow 0-I)$
Pattern	$\geq 2$	$Pna2_1$	The $V_0$ at an O-I site can hop between O-I and O-II sites
(b)			alternatively with one kind of barrier energy.
			$(O-I \rightarrow O-II \rightarrow O-I \rightarrow O-II \rightarrow O-I)$
Pattern	$\geq 2$	$P2_1/c$ , $Pbca$ , $P2_1/m$ ,	The $V_{\rm O}$ at an O-I site can hop between the O-I sites with one kind
(c)		$Pca2_1$	of barrier energy because this barrier energy is lower than the
			lowest barrier energy between O-I and O-II sites
			$(0-I \rightarrow 0-I \rightarrow 0-I \rightarrow 0-I \rightarrow 0-I)$
Pattern	$\geq 2$	R-3, Gen-01, Gen-02,	The $V_{\rm O}$ should hop between two different kinds of $V_{\rm O}$ sites with at
(d)		Gen-08	least two different kinds of barrier energy.
			$(0-I \rightarrow 0-I \rightarrow 0-II \rightarrow 0-II \rightarrow 0-I)$
Pattern	$\geq 2$	P4/n	The $V_{\rm O}$ at an O-I site should hop between the O-I sites with at least
(e)			two different kinds of barrier energy.
			$(O-I \rightarrow (by E^m_1) \rightarrow O-I \rightarrow (by E^m_2) \rightarrow O-I \rightarrow (by E^m_1) \rightarrow O-I, E^m_1 <$
			$E_{2}^{m}$

Table S4 Additional description for the pattern of the minimum barrier energy which is shown in Fig. S3.

<sup>a</sup> O-*I* is a  $V_0$  site with the lowest energy, and O-*II* is another site with the second lowest energy.



Fig. S4 Radial distribution functions according to O–Zr distances of the 30 crystal structures from *reoptimized-ZrO*<sub>2</sub> and *generated-ZrO*<sub>2</sub>. From the bottom to the top, the relative  $\Delta E_f$  (compared with that of the ground-state  $P2_1/c$  structure) of crystal structures increase.

Crystal Structure	<b>x</b> (Å)	<b>y</b> (Å)	z (Å)	α (°)	<b>β</b> (°)	γ (°)	Number of atoms
$P4_2/nmc$	3.626	3.626	5.174	90.00	90.00	90.00	2 Zr, 4 O
Gen-08	10.420	3.651	3.655	90.02	89.85	90.21	4 Zr, 8 O

Table S5 Lattice parameters of unit-cells [Fig. 9(a) and (b)] of two crystal structures of ZrO<sub>2</sub>.



**Fig. S5** Phonon dispersion curves of (a) tetragonal fluorite  $(P4_2/nmc)$  and (b) cubic fluorite (Fm-3m) structures of ZrO<sub>2</sub>.