Supporting Information for

Anisotropic Chemical Strain in Cubic Ceria due to Oxygen-Vacancy-Induced Elastic Dipoles

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Section S1. Derivation of Strain Tensor Using Elastic Dipole Tensor

The chemical strain tensor at a given dilute oxygen vacancy concentration can be calculated by minimizing the total energy, ΔE_{total} with respect to the applied stain. ΔE_{total} consists of the energy due to local lattice distortion caused by oxygen vacancy formation, ΔE_{short} and the long-range elastic strain energy caused by oxygen vacancy formation, ΔE_{long}, as:

$$\Delta E_{total} = \Delta E_{short} + \Delta E_{long} = \frac{\delta}{V_U} G{:}\varepsilon + \frac{1}{2}(C{:}\varepsilon){:}\varepsilon$$

where V_U is the volume per formula unit of perfect CeO_2 and C is the elastic stiffness tensor for the perfect lattice. Taking the derivative of Equation 4 with respect to ε yields:

$$\frac{d\Delta E_{total}}{d\varepsilon} = \frac{d\Delta E_{short}}{d\varepsilon} + \frac{d\Delta E_{long}}{d\varepsilon} = 0$$

$$\frac{d\Delta E_{total}}{d\varepsilon} = 0 = \frac{\delta}{V_U} G + C{:}\varepsilon$$

$$\frac{d\Delta E_{short}}{d\varepsilon} = \frac{d}{d\varepsilon}\left(\frac{\delta}{V_U} G{:}\varepsilon\right) = \frac{\delta}{V_U} G$$

$$\frac{d\Delta E_{long}}{d\varepsilon} = \frac{1}{2}\frac{d}{d\varepsilon}\{(C{:}\varepsilon){:}\varepsilon\} = \frac{1}{2}\left\{\frac{d(C{:}\varepsilon)}{d\varepsilon}\right\}{:}\varepsilon + \frac{1}{2}(C{:}\varepsilon){:}\frac{d\varepsilon}{d\varepsilon}$$

$$\frac{d\Delta E_{long}}{d\varepsilon} = \frac{1}{2}\left\{C{:}\frac{d\varepsilon}{d\varepsilon}\right\}{:}\varepsilon + \frac{1}{2}(C{:}\varepsilon){:}\frac{d\varepsilon}{d\varepsilon} = \frac{1}{2}(C{:}\varepsilon) + \frac{1}{2}(C{:}\varepsilon) = C{:}\varepsilon$$

$$\frac{d\Delta E_{total}}{d\varepsilon} = \frac{\delta}{V_U} G + C{:}\varepsilon = 0$$

$$\varepsilon = \frac{-\delta\left(C^{-1}G\right)}{V_U}$$

Section S2. PDOS Calculations for Stoichiometric and Non-stoichiometric Ceria

Partial density of states (PDOS) were calculated for Ce and O atoms in perfect CeO_2 lattice and shown in Figure S1. Figure S2-S4 show the Ce-*5d* and *4f* orbitals in vacancy containing lattice for two different scenarios. Analysis of PDOS for Ce-*5d* and *4f* orbitals before and after the formation of oxygen vacancy has shown the charge localization in *4f* orbital after $V_O^{\bullet\bullet}$ formation. Electron localization in Ce-*4f* orbital observed in Figure S3 is consistent with previous computational studies.

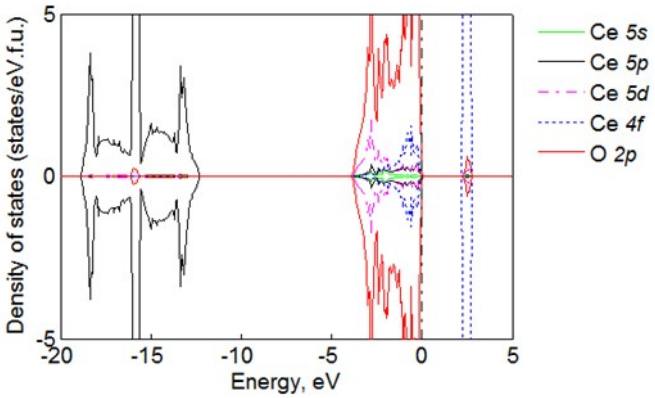

Figure S1. Partial density of states plot for Ce-5s, 5p, 5d, 4f and O-2p orbitals in pure CeO_2

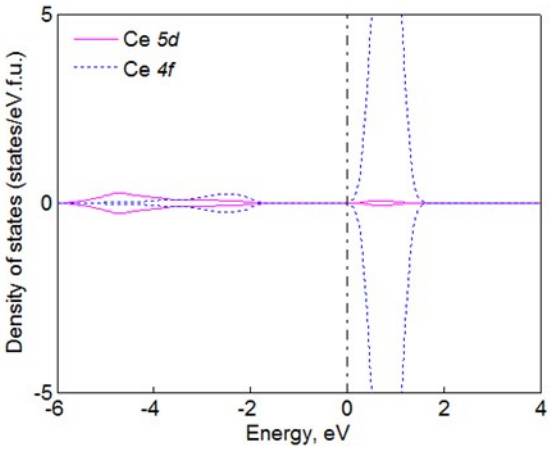

Figure S2. PDOS for Ce^{4+}-5d and Ce^{4+}-4f orbital for Ce^{4+} adjacent to $V_O^{\bullet\bullet}$, after $V_O^{\bullet\bullet}$ formation in asymmetric case. Orbitals show same shape as Ce^{4+} in perfect CeO_2.

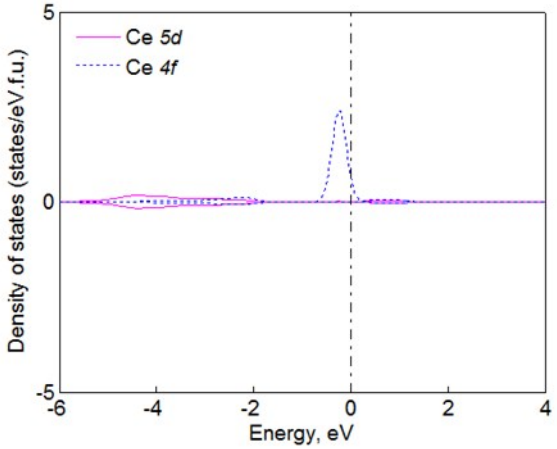

Figure S3. PDOS for Ce^{3+}-5d and Ce^{3+}-4f orbital for Ce^{3+} adjacent to $V_O^{\bullet\bullet}$, after $V_O^{\bullet\bullet}$ formation in asymmetric case. Figure shows localization of excess electron in 4f orbital.

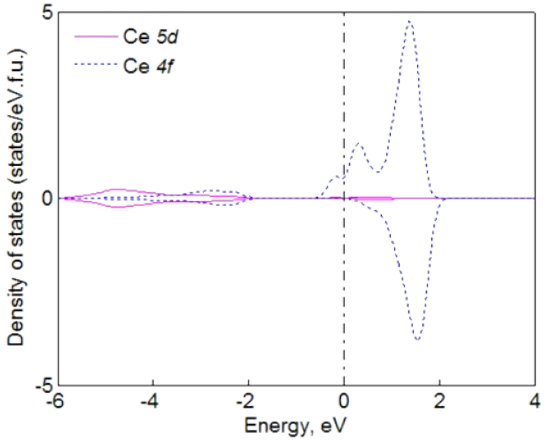

Figure S4. PDOS for $Ce^{3.5+}$-5d and $Ce^{3.5+}$-4f orbital for $Ce^{3.5+}$ adjacent to $V_O^{\bullet\bullet}$, after $V_O^{\bullet\bullet}$ formation in symmetric case. Figure shows localization of excess electron in 4f orbital. This scenario is computational artifact as the structure was energetically unfavorable.

Section S3. Elastic Dipole Moment Calculation

Dipole moment $\vec{p} = \sum_i q_i d_i$

q_i = charge on the ith particle

d_i = displacement of the ith particle

If we assume mean charge as 3.5+ then charge on Ce^{3+} is 0.5 e and the charge on Ce^{4+} is -0.5 e.

Therefore, displacement of Ce atoms from oxygen vacancy center:

vectors	x-comp	y-comp	z-comp	||d||
Ce4+	1.4846	-1.4846	-1.4658	2.5606
Ce4+	-1.4846	1.4846	-1.4658	2.5606
Ce3+	-1.4488	-1.4488	1.4665	2.5196
Ce3+	1.4488	1.4488	1.4665	2.5196

Vector sums			
Ce4+	0.0000	0.0000	-2.9316
Ce3+	0.0000	0.0000	2.9331

Resultant	qi*di		
0.0000	0.0000	2.9323	eÅ
	$\vec{p}$	14.0847	D

1 D (Debye) = 0.20819434 eÅ [https://en.wikipedia.org/wiki/Debye]