Electron Localization Enhances Cation Diffusion in Zirconia and Ceria: A First-Principles Study

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Abstract

According to defect chemistry, the experimental observations of enhanced cation diffusion in a reducing atmosphere in zirconia, ceria and other ceramics support an interstitial mechanism. Yet all computational studies always found a much higher defect formation energy for cation interstitials than for cation vacancies, which on the other hand would rule out the interstitial mechanism. The conundrum has been resolved via first-principles calculations comparing the migrations of reduced cations and fully oxidized ones with their formal charges, in cubic ZrO₂ and CeO₂. Since reduction creates electrons (i.e. cation reduction) and oxygen vacancies at the same time, the latter of which are also highly mobile, we further studied the effect of oxygen vacancy on cation migration. We found in cubic ZrO₂, cation reduction alone
is able to lower the migration barrier, while it is not the case in CeO$_2$; however, a large synergistic effect between cation reduction and oxygen vacancy always holds in both cubic ZrO$_2$ and CeO$_2$, significantly lowering cation’s migration barrier as well as the energy level of localized electron on the migrating cation in the saddle-point state. It signals a negative-$U$ state in which the soft saddle-point environment enables a strong electron-phonon interaction that can over-compensate the on-site Coulomb repulsion. More broadly speaking, this electronic/ionic-defect-mediated ion migration provides a new viewpoint to understand how mass transport controlled by slowest-moving species can be tailored by minor charge carriers—including both oxygen vacancy and electron in the present case—beyond classical nonstoichiometric defect chemistry. These general findings are expected to be applicable to most transitional metal oxides, enabling more genius diffusional control for material processing and device stability.

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I. Introduction

Atomic migration strongly depends on the atomic size because a smaller atom can more easily pass through a crowded saddle point than a larger one. But high-valence cations, while small, are often the slowest diffusing species in ionic crystals. This is seen for $\text{Zr}^{4+}$ in $\text{ZrO}_2$, $\text{Ce}^{4+}$ for $\text{CeO}_2$, $\text{Y}^{3+}$ for $\text{Y}_2\text{O}_3$, and for $\text{Ti}^{4+}$ in $\text{BaTiO}_3$. A reduced cation is larger in size but lower in valence, so it is not obvious whether it migrates faster or slower. Meanwhile, since thermodynamics is also affected by reduction, it may in turn alter defect concentrations and influence diffusivity. For example, for vacancy-mediated cation diffusion (e.g., in zirconia [1-3], zirconia-related oxides of fluorite structure such as ceria [4,5], and perovskites [6,7]), the Law of Mass Action applied to the Schottky reaction predicts lower cation diffusivity upon reduction because the number of oxygen vacancies increases and the number of cation vacancies decreases. These conflicting considerations may be settled by the experimental data, which are rather unambiguous: Reduced cations do have enhanced diffusivity. Specifically, reduction atmospheres enhance sintering [8-10], grain growth [9,11-17], creep, viscoelasticity [18] and alloy mixing/reaction [19], in zirconia [11-13], ceria [8,9,12,14,15,18-20] and other cation-diffusion-limited oxide ceramics [10,16,17]. Therefore, to unravel the competing effects of size, charge and defect concentration and to explain the experimental data, we have studied the defect physics in $\text{ZrO}_2$ and $\text{CeO}_2$, which have applications in exhaust catalysis, gas sensing, and electrochemical energy conversion.
Since the energetics of ionic defects is the focus of this study, it is important to appreciate that it is the Coulomb interaction that holds an ionic crystal together and constitutes most of the internal energy \[21,22\]. Our previous study established that the electrostatic energy is paramount to the stability of zirconia crystals \[1,23\], and we suspect it is even more important in migration. This is because a high-valence cation, while usually well screened in the ground state, is probably poorly screened at the saddle-point state where it is surrounded by much fewer anions. Since it is likely that a reduced saddle-point cation can gain an advantage in this way, we will evaluate this energy advantage of a reduced saddle-point cation despite its increased size using first-principles calculations.

It turns out that two additional effects are also relevant. First, from a practical viewpoint, clearly the most worthwhile case to study is when cation \(M^{z+}\) is the slowest diffusion species, which holds for zirconia (\(Zr^{z+}\)), ceria (\(Ce^{z+}\)), yttria (\(Y^{z+}\)) and several titanates (\(Ti^{z+}\)). Assuming diffusion of other ionic species is also vacancy-mediated, it follows that their vacancies should all migrate much faster. Therefore, \(M^{z+}\) can afford to wait for the arrival of such vacancies (e.g., oxygen vacancies) to see whether they facilitate \(M^{z+}\) migration. This effect could be rather important in \(ZrO_2\) and \(CeO_2\) with their abundant and highly mobile oxygen vacancies. So one model we will study has an oxygen vacancy next to a migrating Zr or Ce cation. Second, we discovered a new effect that manifests in a surprisingly strong tendency for the reduction-created electron to localize at the saddle-point cation. In so doing it lowers the electron energy of the system, which is reminiscent of what is seen at the so-called negative-\(U\) center.
when a second electron in conjunction with a large electron-phonon interaction causes an effectively negative on-site Coulomb energy \((U)\). The outcome of this effect is that it can substantially lower cation’s migration barrier. Although more investigation is clearly needed, we suspect this may well be a rather general circumstance for transition-metal oxides that have no \(d/f\) electron in their un-reduced cations.

II. Methodology

Although lower-valence dopants such as \(Y^{3+}\) and \(Ca^{2+}\) are added to \(ZrO_2\) to provide oxygen vacancies and to stabilize the cubic structure, to simplify the matter, we did not include any dopant but instead started with a metastable cubic structure. We next introduced defects while allowing the size and shape of the supercell to relax, which only caused minor changes in the atomic structure and without leading to any phase transformation. The size and shape of the supercell were kept the same during subsequent calculations for cation migration.

We performed first-principles calculations based on density functional theory (DFT) using the projector augmented-wave (PAW) [24] method within the Perdew-Burke-Ernzerhof (PBE) [25] generalized gradient approximation (GGA) implemented in the Vienna ab initio simulation package (VASP) [26]. The PAW potentials include the following valence electrons: \(5s^24d^2\) for \(Zr\), \(5s^25p^64f^45d^16s^2\) for \(Ce\) and \(2s^22p^4\) for \(O\). We chose a plane-wave cutoff energy of 400 eV and sampled the Brillouin zone using the Monhorst-Pack scheme with a \(3\times3\times3\) \(k\)-point mesh. The DFT+\(U\) approach by Dudarev et al. [27] was used to describe the energy of localized
$d$ electrons of Zr and $f$ electrons of Ce. Specifically, we chose the on-site Coulomb interaction parameter $U$, the on-site exchange interaction parameter $J$, and the effective Hubbard parameter $U_{\text{eff}}=U-J$ as follows: $U=5$ eV, $J=1$ eV and $U_{\text{eff}}=4$ eV for Zr $4d$ states [28-30], $U=5$ eV, $J=0$ eV and $U_{\text{eff}}=5$ eV for Ce $4f$ states [4,31,32]. (Note that Dudarev et al. [27] did not treat $U$ and $J$ independently, only their difference $U_{\text{eff}}=U-J$ is meaningful.) Since these are the most commonly used values for the respective compounds in the literature, our results may be directly compared with the literature results.

All calculations were performed under periodic boundary conditions. In the ground state, we used a $2\times2\times2$ supercell containing 32 Zr or Ce and 64 O. Cation migration was allowed via a vacancy mechanism because the Schottky reaction, having a much lower defect formation energy than cation Frenkel reaction, provides much more cation vacancies than interstitials in ZrO$_2$ [1-3], CeO$_2$ [4,5] and Y-doped ZrO$_2$ [1]. The migrating cation in a supercell of 31 cations and 64 O is situated next to a cation vacancy, a fully charged $V_M^{**}$, $M$ being Zr or Ce, denoted as $V_M$ hereafter. Reduction, when considered, was implemented by providing an extra electron to the supercell. To simulate the migration of a reduced cation, we preselected a target cation and promoted electron localization around it by first displacing the neighboring oxygen ions outward by 0.1-1.0 Å. We then let the system relax to reach convergence (residue atomic forces less than 0.05 eV/Å), which did lead to obvious electron localization as will be shown later. In another model, we included an oxygen vacancy ($V_O^-$, denoted as $V_O$ hereafter) next to the migrating cation, so the supercell contains
31 cations and 63 O.

To track cation migration, the climbing-image nudged-elastic-band (NEB) method [33] implemented in VASP was used with a fixed supercell size and shape. In cubic ZrO$_2$, it determined the migration path and the barrier with the path defined by 7 intermediate states in addition to the initial and final configurations; in CeO$_2$, 3 intermediate states were specified. Convergence for NEB calculations was considered achieved when the residual atomic forces are less than 0.1 eV/Å. After the NEB calculation, static calculations were conducted to calculate the density of state (DOS) and projected density of state (pDOS) on each atom for the ground-state and the saddle-point configurations with a 6×6×6 k-point mesh.

DFT calculations always specify the Fermi level, which is used to determine electron state occupancy. However, to compare electron states in different structural states, such as ground state and saddle-point state, or states with and without one missing $M$ or O, it is convenient if we can find a reference energy level that is relatively insensitive to the structures/defects. All the structures studied here comprise of cation polyhedra bounded by oxygen ions that are (edge-) interconnected into a continuous three-dimensional network. Moreover, their valence bands are mainly made of O2$p$ orbitals. Therefore, we may regard the valence band manifold as representative of network’s electronic states. The overall electronic energy of this network, which is continuous, should be relatively insensitive to isolated structural defects/distortions. In this work, we shall use the valence band maximum as the reference energy to compare electron energies of different structural states.
III. Results

We compare the migration of a fully oxidized cation $M^{4+}$ and a reduced cation $M^{3+}$ ($M$=Zr or Ce), with or without a nearby oxygen vacancy $V_O$, following the four models in Fig. 1a-b (produced by VESTA [34]). The calculated energy profiles during migration are shown in Fig. 1c and the key data for each model are summarized in Table 1.

Figure 1 (a) Schematics of 1×1×1/2 subcell of cubic $MO_2$ ($M$=Zr and Ce) supercell with one cation vacancy $V_M$. $M^{4+}/M^{3+}$ exchanges location with $V_M$ in straight path (black dashed line) when assisted by oxygen vacancy $V_O$ (marked by arrow) or in curved path (red dashed line) when there is no $V_O$; their saddle-point configurations shown on right panel. (b) Schematic migration models. A: $M^{4+}$-$V_M$ exchange without $V_O$. B: $M^{3+}$-$V_M$ exchange without $V_O$. C: $M^{4+}$-$V_M$ exchange with $V_O$. D: $M^{3+}$-$V_M$ exchange with $V_O$. (c) Cation migration energetics along 110 direction for Model A-D.
Table 1 Summary of calculated parameters for $M$-$V_M$ exchange in cubic ZrO$_2$ and CeO$_2$. Compare $M$-O distances with those of ground state: 2.24 Å for Zr-O and 2.36 Å for Ce-O when defect-free, and somewhat shorter distances when $V_M$ is present.

Excluded from Ce’s Bader charge are 8 inner-shell electrons ($5s^25p^6$).

| Material | Model | Path    | Barrier (eV) | Nearest $M$-O distance (Å) | Bader charge on migrating $M$ ($\epsilon$) |
|----------|-------|---------|-------------|----------------------------|------------------------------------------|
|          |       |         |             | Ground state   | Saddle point   | Ground state   | Saddle point   |
| ZrO$_2$  | A     | Curved  | 4.64        | 2.15          | 1.97          | 0.62          | 0.80          |
|          | B     | Curved  | 3.90        | 2.23          | 2.04          | 1.44          | 1.28          |
|          | C     | Straight| 4.31        | 2.15          | 2.05          | 0.59          | 0.68          |
|          | D     | Straight| 3.17        | 2.24          | 2.11          | 1.43          | 1.49          |
| CeO$_2$  | A     | Curved  | 4.32        | 2.27          | 2.03          | 1.63          | 1.74          |
|          | B     | Curved  | 4.79        | 2.39          | 2.12          | 1.91          | 1.92          |
|          | C     | Straight| 3.96        | 2.25          | 2.06          | 1.65          | 1.67          |
|          | D     | Straight| 3.28        | 2.38          | 2.13          | 1.91          | 1.92          |

Model A ($M^{4+}$ migration): This is taken as the base case, which has neither reduction nor $V_0$. The $M^{4+}$-$V_M$ exchange does not follow a straight line. Instead, it veers into a cation-absent neighboring cell to avoid the two oxygen ions in the red dashed curve in Fig. 1a. At the saddle point, $M^{4+}$ is surrounded by six oxygens (Fig. 1a, upper inset); the two pointed by black arrows are closer than the remaining four. Nevertheless, it has the following features, listed in Table 1, that are shared by all four models: (a) Zr being smaller has a shorter Zr-O bond length than Ce-O, (b) Zr is more ionic than Ce judging from the lower Bader charge [35], and (c) the M-O distance is much shorter at the saddle point than at the ground state. The density of state (DOS) is shown in Fig. S1 (ZrO$_2$) and Fig. S3 (CeO$_2$) for both the ground state.
and the saddle-point state.

**Model B** (*M^{3+} migration*): The migration path is similar to that in **Model A**. But as shown in Table 1, an extra electron is now localized at the target (migrating) cation in both the ground state and the saddle-point state, indicated by an increased Bader charge, a larger \(M^{3+}\) than \(M^{4+}\) and a correspondingly longer \(M-O\) distance. The localized electron just beneath the Fermi level in Fig. 2a&d and Fig. 4a&d occupies a “gap state” between the valence band maximum (VBM; mainly O 2p orbitals) and the conduction band minimum (CBM; mainly Zr 4d orbitals or Ce 4f orbitals). It comes from the sharp, narrowly projected density of state (DOS) of the target \(M^{3+}\) (see Fig. 2b&e and Fig. 4b&e). Interestingly, the Bader charge for \(Zr^{3+}\) is larger at the ground state than at the saddle point, which is not found elsewhere in Table 1. This may be understood from the following [23,36]: According to Pauling’s rule (cation/anion radius ratio determines coordination number), in the ground state, \(Zr^{4+}\) (but not the larger \(Ce^{4+}\)) is too small for the 8-oxygen-neighbor environment in the fluorite structure, so it favors acquiring an electron to form a larger \(Zr^{3+}\), thus gaining stability. As the coordination number decreases to 6 at the saddle point, there is no more such need, so some localized electron and Bader charge are shed. This is further verified by the DOS of the gap state: In Fig. 2e it decreases from the ground state to the saddle-point state. Another interesting point is: While \(Ce^{3+}\) encounters a higher migration barrier (4.79 eV) than \(Ce^{4+}\) (4.32 eV), presumably because of the size effect, the migration barrier of \(Zr^{3+}\) (3.90 eV) is actually significantly lower than that of \(Zr^{4+}\) (4.64 eV). This gives the first indication that reducing the cation charge can facilitate
cation migration.

**Model C (V<sub>O</sub>-aided M<sup>4+</sup> migration):** With one intervening lattice oxygen removed, M<sup>4+</sup> now migrates along a straight line experiencing a (~0.35 eV) lower migration barrier than that in **Model A**. Therefore, V<sub>O</sub>, providing more space at the crowded saddle-point configuration, apparently helps cation migration, which may be attributed to the size effect. At the saddle point, M<sup>4+</sup> is surrounded by five oxygens (Fig. 1a, lower inset), the one marked by the arrow is closer than the remaining four. The density of state (DOS) is shown in **Fig. S2** for ZrO<sub>2</sub> and **Fig. S4** for CeO<sub>2</sub>.

**Model D (V<sub>O</sub>-aided M<sup>3+</sup> migration):** Similar to **Model C**, the M<sup>3+</sup>-V<sub>M</sub> exchange is along a straight line. The extra electron is localized at the target cation, which has a larger Bader charge and a longer M-O distance than M<sup>4+</sup> in **Model C** at both the ground state and the saddle-point state (see **Table 1**). Compared to **Model B**, the barrier is lower by 0.73 eV in ZrO<sub>2</sub> and 1.51 eV in CeO<sub>2</sub>, suggesting a very significant size effect due to V<sub>O</sub> that is especially important in CeO<sub>2</sub>. But the charge effect is equally significant: Compared to **Model C**, the barrier is lower by 1.14 eV in ZrO<sub>2</sub> and 0.68 eV in CeO<sub>2</sub>, so lowering the valence of cation is especially important in ZrO<sub>2</sub>.

To understand this result better, we refer to **Fig. 3b&c** and **Fig. 5b&c**, which show that the lower barrier mainly comes from the much lower gap-state energy at the saddle-point: The gap state is now much closer to the VBM, and in the case of Ce<sup>3+</sup> (**Fig. 5b&c**) it already merges into the valence band (O 2p orbitals). Compared to that of the ground state, the gap-state energy of the saddle-point is lower by about 1.5 eV.
in Zr$^{3+}$ and 1.2 eV in Ce$^{3+}$. Naturally, with such pronounced energy lowering in ZrO$_2$, there is no need to shed electron when Zr$^{3+}$ goes to the saddle point. So the Bader charge of Zr$^{3+}$ does not decrease in Model D, unlike in Model B.

The size effect and the charge effect here are actually synergistic. If the two effects are additive, we should expect the barrier lowering from Model A→B (the charge effect due to one additional electron) and from Model A→C (the size effect due to one additional V$_0$) add up to 1.07 eV for ZrO$_2$ and −0.11 eV for CeO$_2$. But the lowering from Model A→D is much larger: 1.47 eV for ZrO$_2$ and 0.94 eV for CeO$_2$. The synergism is understood as follows: Although the removal of one lattice oxygen creates a more open pathway, it also leaves the migrating cation less screened, which raises the electrostatic energy that offsets the beneficial size effect. However, after first localizing an extra electron at the migrating cation to lower its electrostatic energy, the cation can more fully utilize the advantage of the more open space. The combination of the size effect, the charge effect and the synergistic effect lowers the migration barrier for Zr$^{3+}$ to 3.17 eV in Model D from 4.64 eV (for Zr$^{4+}$) in Model A, and correspondingly in ceria to 3.28 eV from 4.32 eV. Since mobile oxygen vacancies are readily available in these oxides, Model D is realistic, and such large energy reduction in cation migration barrier can be expected in reduced zirconia and ceria.
Figure 2 Calculated density of states (DOS) for Model B in zirconia. Ground state: (a) total DOS, (b) projected DOS of target Zr (in green) and nearest O (in red), and (c) projected DOS of reference Zr (in green) and O (in red) away from migration path. Saddle-point state: (d) total DOS, (e) projected DOS of migrating Zr (in green) and nearest O (in red), and (f) projected DOS of reference Zr (in green) and O (in red). Zero energy is set at Fermi level and spin-up and spin-down states are plotted as positive and negative DOS, respectively. The reference Zr and O in (c) and (f) are both outside the half supercell shown in Fig. 1a.
Figure 3 Calculated density of states (DOS) for Model D in zirconia. Ground state: (a) total DOS, (b) projected DOS of target Zr (in green) and nearest O (in red), and (c) projected DOS of reference Zr (in green) and O (in red) away from migration path. Saddle-point state: (d) total DOS, (e) projected DOS of migrating Zr (in green) and nearest O (in red), and (f) projected DOS of reference Zr (in green) and O (in red). Zero energy is set at Fermi level and spin-up and spin-down states are plotted as positive and negative DOS, respectively. The reference Zr and O in (c) and (f) are both outside the half supercell shown in Fig. 1a.
Figure 4 Calculated density of states (DOS) for Model B in ceria. Ground state: (a) total DOS, (b) projected DOS of target Ce (in blue) and nearest O (in red), and (c) projected DOS of reference Ce (in blue) and O (in red) away from migration path. Saddle-point state: (d) total DOS, (e) projected DOS of migrating Ce (in blue) and nearest O (in red), and (f) projected DOS of non-participating reference Ce (in blue) and O (in red). Zero energy is set at Fermi level and spin-up and spin-down states are plotted as positive and negative DOS, respectively. The reference Ce and O in (c) and (f) are both outside the half supercell shown in Fig. 1a.
Figure 5 Calculated density of states (DOS) for Model D in ceria. Ground state: (a) total DOS, (b) projected DOS of target Ce (in blue) and nearest O (in red), and (c) projected DOS of reference Ce (in blue) and O (in red) away from migration path. Saddle-point state: (d) total DOS, (e) projected DOS of migrating Ce (in blue) and nearest O (in red), and (f) projected DOS of non-participating reference Ce (in blue) and O (in red). In each figure, zero energy is set at Fermi level and spin-up and spin-down states are plotted as positive and negative DOS, respectively. The reference Ce and O in (c) and (f) are both outside the half supercell shown in Fig. 1a.
IV. Discussion

(1) Reduction enhanced cation diffusion: defect chemistry and beyond

As described in the Introduction, reduction can definitely enhance cation diffusion in zirconia, ceria and related oxides. Our study revealed that the cation migration barrier is lowered by both reduction and $V_O$. In these oxides, there are abundant $V_O$ (because of the presence of many acceptor donors, e.g., Ca$^{2+}$, Y$^{3+}$ and Gd$^{3+}$) that are fast-diffusing (with a migration barrier of only $\sim 0.5$ eV), Model C and in particular Model D are obviously preferred. We believe Model C should prevail in an oxidizing atmosphere, in which a $V_M$ waits until it is surrounded by a $V_O$ before it engages in a $V_M-M^{4+}$ exchange. In a highly reducing atmosphere, Model D should prevail, in which a $V_M$ waits until it is surrounded by a $V_O$ and an electron arrives at a neighboring $M^{4+}$ before it engages in a $V_M-M^{3+}$ exchange. Since the concentration of cation vacancies is extremely low, the above picture should hold even with a dilute concentration of electrons and O vacancies, which is likely to be the case of pure ceria.

We can now make a quantitative estimate of diffusivity enhancement. Without reduction, the cation diffusivity is proportional to $[M^{4+}][V_M] \exp\left(-\frac{\text{Barrier of } M^{4+}}{k_B T}\right)$ where $[M^{4+}]$ is set to be 1; with reduction, it is proportional to $[M^{3+}][V_M] \exp\left(-\frac{\text{Barrier of } M^{3+}}{k_B T}\right)$. Therefore, the enhancement factor due to

$$\frac{[M^{3+}][V_M] \exp\left(-\frac{\text{Barrier of } M^{3+}}{k_B T}\right)}{[M^{4+}][V_M] \exp\left(-\frac{\text{Barrier of } M^{4+}}{k_B T}\right)}$$
reduction is \[
\left\{ [M^{3+}] \exp\left(-\frac{\text{Barrier of } M^{3+}}{k_B T}\right) \right\} \bigg/ \left\{ [M^{4+}] \exp\left(-\frac{\text{Barrier of } M^{4+}}{k_B T}\right) \right\}.
\]
The ratio \[
\exp\left(-\frac{\text{Barrier of } M^{3+}}{k_B T}\right) \bigg/ \exp\left(-\frac{\text{Barrier of } M^{4+}}{k_B T}\right)
\]
is just \[
\exp\left(\frac{\Delta E}{k_B T}\right),
\]
where \(\Delta E\) is the barrier difference in Model C and D. This ratio is larger for Zr than for Ce (1.14 eV in ZrO\textsubscript{2} and 0.68 in CeO\textsubscript{2}). The other ratio \([M^{3+}]/[M^{4+}]\) is obtained using the thermodynamic data of the reaction \(O^*_O = 2e^+ + V_o^{*o} + \frac{1}{2}O_2\). Assuming all the electrons are localized at cations, it gives a \([M^{3+}]/[M^{4+}]\) ratio that is much larger for ceria than for zirconia, hence dominating the enhancement factor as illustrated in the example below: At 1200 °C and an oxygen partial pressure of \(10^{-10}\) atm, 8 mol% yttria stabilized zirconia \(\text{Zr}_{0.852}\text{Y}_{0.148}\text{O}_{1.926}\) has an oxygen nonstoichiometry of \(8.6\times10^{-5}\) (hence \([e]/[M^{4+}] = 1.7\times10^{-4}\) according to [37]), so with \(\Delta E=1.14\) eV for zirconia the overall enhancement factor is 1.8. Under the same condition, 10 mol% Gd-doped ceria \(\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}\) has a nonstoichiometry of 0.1 (hence \([e]/[M^{4+}] = 0.2\) according to [38]), so even though with a smaller \(\Delta E=0.68\) eV for ceria the overall enhancement factor of 42 is actually bigger. Therefore, reduction enhanced cation diffusion should be more pronounced in ceria than in zirconia ceramics.

The above finding is supported by experimental observations. (a) Under 5% H\textsubscript{2}, the grain boundary mobility of yttria-stabilized zirconia (both tetragonal and cubic forms) increases by only \~2 times relative to that in air [12], possibly due to a dilute \([\text{Zr}^{3+}]\). However, a severe electrochemical reduction at 1200 °C can push the population of \([\text{Zr}^{3+}]\) much higher to realize a >1,000 times increase in the grain boundary mobility [11-13]. (At 1200 °C \(\exp(\Delta E/k_B T)=7,954\) for zirconia according to
Undoped ceria can be easily reduced because Ce$^{3+}$ is relatively stable. So its grain boundary mobility in air is already ~2 times that in pure oxygen [14], where [Ce$^{3+}$] is expected to be small. In Gd-doped ceria, 5% H$_2$ increases the grain boundary mobility by ~400 times over that in air [12], where [Ce$^{3+}$] may already be saturated. (For ceria, exp($\Delta E/k_BT$)=212 at 1200 °C.) Enhanced sintering [8,9], creep [18], viscoelastic property [19], and cation inter-diffusion [20] have also been reported in ceria under a reducing condition. (3) When ceria-stabilized tetragonal zirconia (with 12 mol % CeO$_2$) is additionally modified by 1 mole percent DO$_x$, with $D$ a dopant cation with valence from $+2$ (Ca, Mg) to $+3$ (Y, Yb, In, Sc) to $+4$ (Ce, Ti) to $+5$ (Ta, Nb) and correspondingly $x$ varying from 1 to 2.5, the grain boundary mobility in air increases in the same order. [39] This may be explained by the increasing [Ce$^{3+}$], which provides the extra electrons that can go around and promote $M^{2+}$ migration. Moreover, ceria-stabilized tetragonal zirconia has a larger grain size (2 μm) than yttria-stabilized tetragonal zirconia (0.2 μm, having 2 and 2.5 mole percent Y$_2$O$_3$, beyond the later cubic zirconia will appear) presumably because of Ce$^{3+}$-promoted Zr$^{3+}$ migration.

(2) Ionics: size/charge effects and beyond

Conventional theory of ionic bonding stresses the central influence of the Madelung energy with which all the energies should scale. Nevertheless, we see definitive evidence for the size effect in the change of the migration path from a curved one to a straight one in the presence of a V$_O$. Comparing Model A and C, we
estimate $V_0$ lowers the migration barrier by 0.33 eV for Zr$^{4+}$ and 0.36 eV for Ce$^{4+}$; comparing Model B and D, it is 0.73 eV for Zr$^{3+}$ and 1.51 eV for Ce$^{3+}$. Therefore, the size effect is more pronounced for $M^{3+}$ and especially for Ce$^{3+}$, which is understandable because Ce$^{3+}$ is larger than Zr$^{3+}$, whereas both Zr$^{4+}$ and Ce$^{4+}$ are much smaller.

The above cannot be the full story, however. This becomes clear if we compare Zr$^{3+}$ and Y$^{3+}$, which like Zr$^{3+}$ is larger in size and lower in (nucleus) valence than Zr$^{4+}$, but unlike Zr$^{3+}$ it shares the same electronic configuration as Zr$^{4+}$ ($d^0$). Yet it has a comparable diffusivity to that of Zr$^{4+}$. (Tracer diffusion [40,41] give a Y$^{3+}$ diffusivity that is 2.5-4.3 times that of Zr$^{4+}$. Such kinetic advantage should lead to Y segregation at the cathode in electro-diffusion, but Y$^{3+}$ actually segregates at the anode instead. [42] The latter observation sets an upper bound of Y$^{3+}$ diffusivity at 4/3 times that of Zr$^{4+}$.) In contrast, Zr$^{3+}$ diffuses $10^3$-$10^4$ times faster than Zr$^{4+}$ according to our grain growth study [11-13]. To explain the huge diffusivity difference between Zr$^{3+}$ and Y$^{3+}$, we must identify a very large electronic effect going beyond the valence and size consideration that are comparable for Y$^{3+}$ and Zr$^{3+}$.

Electronically, Zr$^{3+}$ differs from Y$^{3+}$ in that it alone has an outer shell electron, of the $4d^1$ configuration. This outer shell electron is indeed localized around the target Zr: The projected DOS (Fig. 2 and 3) illustrate that the target Zr can hold onto the extra $4d$ electron in the journey of migration—from the ground state through the saddle point. The same is also true for Ce, which holds onto its extra $5f$ electron (Fig. 4 and 5). Clearly, there must be an energetic advantage to have electron localization, which
is verified in our calculation: If the extra electron in the supercell is not localized around the target cation in Fig. 1a but added to the (Zr4d or Ce5f) conduction band of the reference Zr or Ce outside the half-supercell shown in Fig. 1a, then the electron energy would be at least 2 eV higher. (Compare the energy of the gap state and that of the reference Zr or Ce in Fig. 2-5.). This point and its relevance to cation migration is further made clear in Fig. 6, which summarizes the energies of the gap state and CBM relative to VBM in Fig. 2-5, for all the cation locations including at both the ground state and the saddle-point state. The extra electron added always enjoys an energy lowering (marked by an arrow in Fig. 6) (a) when it is localized at the target cation, (b) when the target cation is moved from the ground state to the saddle-point state, and (c) where Vo provides more free volume and a softer local environment as in Model D, such energy lower is especially large. This energy lowering is at the heart of the lowered migration barrier, and it is clearly a quantum mechanical effect outside the classical size/charge consideration.

Figure 6 Electron levels in ZrO2 and CeO2 of cations in Model B and D relative to energy reference at VBM. Extra electron is added to reference cation (outside half
supercell shown in Fig. 1a) at CBM, to target cation at ground-state lattice location at $M^L$, and to target cation at saddle-point location at $M^{SD}$.

(3) **Negative $U$ center** [43]

Our calculation used the DFT+$U$ method to account for the strong on-site Coulomb repulsion (the Hubbard $U$. [43]) between $d/f$ electrons. This is needed to obtain the correct conduction band of overlapping Zr4$d$ and Ce4$f$ electrons. The term also explains why a small polaron [44,45] forms when an additional electron is introduced to ZrO$_2$ and CeO$_2$: It is localized at one cation site instead of spreading into the conduction band, because the latter would require two electrons from two neighboring cations to overlap thus paying for $U$. Our calculation further illustrated that such localization yields an energetic advantage, in that the occupied state being a gap state lies below the CBM, and especially so when the cation is at the saddle point. This is the fundamental reason why reduction lowers the migration barrier in vacancy-mediated cation diffusion.

Our results may be understood as follows. When the site symmetry of the cation is progressively lowered, from the ground state to the saddle-point state, and to the state of having a neighboring V$_0$, the tendency for localization and energy-lowering strengthens. This is especially true for ceria that has spatially narrower 4$f$-electrons compared to zirconia’s 4$d$-electrons. (Indeed, $U_{\text{eff}}$ used for Ce is larger than for Zr.) Previous studies have shown that once the gap state falls below the mid-gap, it will increasingly acquire the O2$p$ character of the valence band. [32] This is also the case
in our study. For example, the DOS of O2$p$ in Fig. 5e accentuates at the localization energy. From this, a simple picture emerges: The localized electron of distorted $M^{3+}$ resonates with the O2$p$ electrons. In terms of molecular orbitals, the empty conduction band with undistorted $M^{4+}$ in these compounds is made of the lowest $d/f$ orbitals, but their degeneracy is lifted by symmetry-breaking distortions, which creates new molecular orbitals that lie closer to the VBM and may thus more favorably hybridize with VBM’s O2$p$ orbitals. Such is the nature of the gap state in Fig. 3e, 4e and 5e, and why it leads to a very substantial reduction of migration barrier and a very pronounced enhancement of cation diffusion in a reducing atmosphere.

We now suggest a broader view to understand the above results. As an extra electron is added to a multi-electron system, it generally increases the energy for two reasons. (1) When the electron converts a one-electron state to a two-electron state, the energy increases by the Hubbard $U$, which is due to the on-site two-electron repulsion. (2) When all the lower-energy electron states are already occupied, the electron must occupy a higher energy state. For $M^{4+}$, adding an extra electron nominally requires $E_g$, the energy gap between CBM and VBM, which is the case when the electron is added to a reference $M^{4+}$ outside the half-supercell depicted in Fig. 1a. We propose that, empirically, we may also regard $E_g$ as the system $U$, defined as the energy to add one extra electron to a multi-electron system. Then any site that offers a smaller $U$ offers a more favored site for the extra electron, and in the extreme case when the extra electron actually occupies a state below VBM, the empirical $U$ thus defined is negative and the site is a “negative-$U$” site. Inasmuch as all the
low-symmetry $M^{4+}$ sites in Fig. 2-5 offer the extra electron a gap state, they are all favored sites. But in Fig 5e, the saddle-point $M^{4+}$ with a neighboring $V_O$ (Model D) is actually a negative-$U$ site. (See this more clearly in the right-most panel of Fig. 6.) We recall that the negative-$U$ concept is usually reserved for case (1), and it was first proposed for amorphous chalcogenides that have highly distorted local structures, low elastic moduli and large electronic polarizabilities, so much so that the introduction of an extra electron can easily distort the lattice to relax the structure, hence lowering the system energy and converting the positive pairing $U$ to a negative $U$. Although it does not involve electron pairing, our findings are qualitatively consistent with the above picture, in that the energy lowering of the gap state becomes more pronounced as the symmetry lowers (from lattice-site ground-state to interstitial-site saddle-point state), the modulus decreases (ceria is softer than zirconia, and $V_O$ further lowers the local modulus), and the polarizability increases (ceria is more polarizable than zirconia). In the extreme case when all the above conditions are met, it too produces “negative-$U$” states (in our definition) in the case of Model D in ceria.

The above results may be further understood as follows. The saddle-point configuration is elastically soft and fluid; indeed, by definition, a “saddle” point has a negative elastic modulus along the migration direction. So the additional electron that may require atomic displacement nearby to hybridize with $O2p$ orbitals can induce such displacement rather easily. Such displacement may be regarded as a form of static electron-phonon interaction, favored by polarization but countered by elasticity. If on balance the new electronic and atomic configuration lowers the overall energy, a
negative $U$ state results. This is easier to achieve when O2p hybridization is easier (which is the case with the smaller band gap of CeO$_2$, and with lower symmetry as at the saddle point) and when a neighboring $V_0$ is present (Model D).

The synergistic diffusion-enhancing effect of reduction and lattice vacancy in zirconia and ceria is thus understood. Beyond it, we believe our findings are likely generalizable to other ionic compounds, especially to those that have cations of $d^0$ or $f^0$ electronic configuration. These compounds also have full VB and empty CB, and a gap state must appear when their cation enters a saddle-point location and with a nearby cation/anion vacancy. Indeed, these are often the ferroelectric compounds, whose propensity for lattice distortion and a soft mode is also attributed to a similar electronic origin. (According to John Goodenough, distortion lowers the VBM and raises the CBM, which lowers the overall electronic energy for any $d^0$ or $f^0$ system.) Specifically, we expect reduction and any additional cation/anion vacancy will enhance vacancy-mediated migration of the rate-limiting cation. Our preliminary calculations on perovskite systems seem to support this proposal.

V. Conclusions

(1) According to first-principles calculations, the migration barrier next to an oxygen vacancy and a cation vacancy is 3.17 eV for Zr$^{3+}$ in cubic ZrO$_2$ and 3.28 eV for Ce$^{3+}$ in CeO$_2$. They are considerably lower than the barriers for tetravalent cations, and can explain why cation diffusion in fluorite structure oxides is enhanced under reducing atmospheres.
(2) Enhanced migration is mostly due to an electronic effect. The size effect attributed to oxygen vacancy alone is quite small, but it has synergism with the electronic effect when the cation captures an extra electron, which occupies an especially low energy state at the saddle point thus lowering the overall migration barrier. Such low energy state is available around the saddle-point cation because of orbital level splitting, better hybridization with O2p, and the flexibility of the soft local environment that permits lattice distortion to optimize hybridization.

(3) The electronic effect on enhanced cation migration becomes more pronounced in fluorite structure oxides when the oxides are more easily reducible. This is the case for CeO2 and when zirconia is doped with Ce or with donor cations. The electronic effect is akin to associating the saddle-point cation with a negative-\(U\) center with, and such effect may be expected in other transition metal oxides, especially when their rate-limiting cations have \(d^0\) or \(f^0\) electronic configuration.

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Supplementary information

Figure S1 Calculated density of states (DOS) for Model A in zirconia. Ground state: (a) total DOS, (b) projected DOS of target Zr (in green) and nearest O (in red), and (c) projected DOS of reference Zr (in green) and O (in red) away from migration path. Saddle-point state: (d) total DOS, (e) projected DOS of migrating Zr (in green) and nearest O (in red), and (f) projected DOS of reference Zr (in green) and O (in red). In each figure, zero energy is set at Fermi level and spin-up and spin-down states are plotted as positive and negative DOS, respectively. The reference Zr and O in (c) and (f) are both outside the half supercell shown in Fig. 1a.
Figure S2 Calculated density of states (DOS) for Model C in zirconia. Ground state: (a) total DOS, (b) projected DOS of target Zr (in green) and nearest O (in red), and (c) projected DOS of reference Zr (in green) and O (in red) away from migration path. Saddle-point state: (d) total DOS, (e) projected DOS of migrating Zr (in green) and nearest O (in red), and (f) projected DOS of reference Zr (in green) and O (in red). In each figure, zero energy is set at Fermi level and spin-up and spin-down states are plotted as positive and negative DOS, respectively. The reference Zr and O in (c) and (f) are both outside the half supercell shown in Fig. 1a.
Figure S3 Calculated density of states (DOS) for Model A in ceria. Ground state: (a) total DOS, (b) projected DOS of target Ce (in blue) and nearest O (in red), and (c) projected DOS of reference Ce (in blue) and O (in red) away from migration path. Saddle-point state: (d) total DOS, (e) projected DOS of migrating Ce (in blue) and nearest O (in red), and (f) projected DOS of non-participating reference Ce (in blue) and O (in red). In each figure, zero energy is set at Fermi level and spin-up and spin-down states are plotted as positive and negative DOS, respectively. The reference Ce and O in (c) and (f) are both outside the half supercell shown in Fig. 1a.
**Figure S4** Calculated density of states (DOS) for **Model C** in ceria. Ground state: (a) total DOS, (b) projected DOS of target Ce (in blue) and nearest O (in red), and (c) projected DOS of reference Ce (in blue) and O (in red) away from migration path. Saddle-point state: (d) total DOS, (e) projected DOS of migrating Ce (in blue) and nearest O (in red), and (f) projected DOS of non-participating reference Ce (in blue) and O (in red). In each figure, zero energy is set at Fermi level and spin-up and spin-down states are plotted as positive and negative DOS, respectively. The reference Ce and O in (c) and (f) are both outside the half supercell shown in Fig. 1a.
