Is excess faster than deficient? A molecular-dynamics study of oxygen-interstitial and oxygen-vacancy diffusion in CeO₂

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Abstract

The diffusivity of oxygen interstitials (D_i) and of oxygen vacancies (D_v) in fluorite-structured CeO₂ was studied by means of classical molecular dynamic simulation techniques. Simulations were performed on cells that were either oxygen abundant or oxygen deficient at temperatures 1500 ≤ T / K ≤ 2000 for defect site fractions 0.18% ≤ n_i/v ≤ 9.1%. In general, we found that at a given temperature T and defect site fraction n_i/v, the vacancy diffusivity D_v was higher than the interstitial diffusivity D_i. Isothermal values of D_i and D_v were constant at low defect site fractions (n_i/v < 0.91%), but the behaviour diverged at higher n_i/v, whereas D_v decreased at higher n_i, D_i increased at higher n_i. The analysis also yielded, as a function of n_i/v, activation enthalpies (ΔH_mig) and entropies (ΔS_mig) of vacancy migration and of interstitial migration. A constant value of ΔH_mig,i ≈ 0.6 eV was found for low n_i, with increases in ΔH_mig,i observed for n_i > 0.91%. For low n_i, a constant value of ΔH_mig,i ≈ 1.4 eV was found, with a surprising decrease in ΔH_mig,i for n_i > 0.91%. The effect of dopants on the behaviour of the defect diffusivities was also studied. Doping with Gd³⁺ had a detrimental effect on vacancy diffusion, with a slight decrease in D_v and an increase in ΔH_mig,i being observed. Donor doping with Nb⁵⁺, in contrast, was beneficial, resulting in higher D_i and a decrease in ΔH_mig,i. We suggest that the migration mechanism of oxygen interstitials in CeO₂, non-collinear interstitialcy, is responsible for the lower defect diffusivity and higher migration barrier.

1. Introduction

In the majority of oxide-ion conducting crystalline solids, it is the migration of oxygen vacancies that is responsible for the ionic conductivity [1–14]. The alternative—the migration of oxygen interstitials—is known for a few selected materials (e.g. for the Ruddlesden–Popper La₃NiO₄₋₀.₅ [15, 16]; for the apatite-based La₁₀Ge₆O₂₇ [17] and La₁₀Si₆O₂₇ [18]; and for the cage compound Ca₁₂Al₁₂O₃₃, mayenite [19–22]), but these are isolated examples. In general, far less attention has been devoted to such interstitial-dominated systems. It is therefore unclear if such interstitial-dominated systems can provide superior active materials for electrochemical applications, such as Solid Oxide Fuel Cells (SOFC), Solid Oxide Electrolyser Cells (SOEC), Oxygen Permeation Membranes (OPM), Reversible Oxide Batteries (ROB) or Resistive Switching RAM (ReRAM).

At the most basic level the process of ion migration in an ionic solid consists of a charged particle moving within a lattice of other charged particles. On this basis there appears to be no reason why oxygen interstitials should on principle be either far less mobile or far more mobile than oxygen vacancies [14]. One class of materials, for which both cases have been studied, is the family of AO₂ fluorite-structured oxides, such as ZrO₂, HfO₂, CeO₂, ThO₂, UO₂ and PuO₂. Most of the published computational studies on these materials, however, only report activation barriers for oxygen-vacancy migration (from static calculations either based on density-functional-theory calculations [23–29] or based on empirical pair-potentials calculations [30–35]). The activation barrier for vacancy migration is predicted to be in the range of 0.4 eV to 0.6 eV. For the few studies, in
which oxygen-interstitial migration has been examined, higher values are reported, in the range of 0.8 eV to 1.1 eV [25, 36–41] (with the exception of HfO₂, for which a barrier of 1.8 eV is reported [42]).

There have been attempts in the literature to compare interstitial and vacancy transport in oxides [1, 11, 12, 14, 16, 43], but they deal with the subject neither systematically nor in depth. In this study, taking the cubic (high-symmetry, isotropic) oxide CeO₂ as our model AO₂ system, we examine systematically the question of which point-defects (oxygen interstitials or oxygen vacancies) exhibit the higher diffusivity. To this end, we employ molecular dynamics (MD) simulation techniques, as they give us, from data obtained as a function of temperature, not only the activation enthalpies (ΔH_mig) and entropies (ΔS_mig) of migration, but also absolute values for the diffusion coefficients. In particular, we compare the defect diffusivities D_{i/v} as a function of defect site fraction n_{i/v}; since D_{i/v} should be independent of n_{i/v} for dilute solutions, deviations from this behaviour allows us to study defect–defect self-interactions and to determine the defect concentration up to which the dilute solution treatment is still applicable, as far as point-defect migration is concerned. Lastly, we look at the influence of dopants on the oxygen-interstitial and oxygen-vacancy diffusivity. To this end we introduce Nb⁵⁺ or Ta⁵⁺ as donor dopants; or we introduce Gd³⁺ as an acceptor dopant; and we compare the results with those obtained for the dopant-free cells.

2. Computational section

The system is described by short-range interactions with a Buckingham potential and long-range coulombic interactions. Full ionic charges are assumed. The set of pair-potential parameters derived by Sayle et al [44] for CeO₂ have already been used to simulate structures and properties of extended defects [44, 49], activation barriers of oxygen-vacancy migration in pristine [30] and in strained [32] CeO₂ and non-linear oxygen-vacancy mobility in CeO₂ [35]. The cation–anion parameters used in this study were all derived for Catlow’s oxygen–oxygen interaction [45] and should therefore be compatible with one another. The inter-cationic interactions, with the exception of coulombic interactions, were assumed to be zero. The set of potential parameters used in our simulations is given in table 1.

In this study, simulations of bulk CeO₂ employed a cell of dimensions 14a × 14a × 14a (where a is the lattice parameter of cubic CeO₂), containing 32928 ions, i.e. Ce₁₀₉₇₆O₂₁₉₅₂. We performed two different sets of simulations. In the first set, we randomly introduced vacancies or interstitials throughout the cell and compensated the charge with a uniform background charge. We refer to these simulation cells as bgcc (background charge-compensated); they allow us to study the diffusion behaviour of the two oxygen defects, free from the interactions with compensating defects [29, 50–52]. The second set of simulations were performed on cells containing dopant ions to charge compensate the respective oxygen point-defects; donor dopants (Nb⁺⁶Ce or Ta⁺⁵Ce) for the cells containing oxygen interstitials (O⁺) and acceptor dopants (Gd⁺³Ce) for the cells with oxygen vacancies (V⁰). The dopants were randomly distributed over the possible cation sites replacing regular Ce⁺³. Between 20 to 1000 oxygen interstitials or oxygen vacancies were introduced into the simulation cell: this corresponds to defect site fractions between 0.18% to 9.11% for the interstitials and 0.09% to 4.56% for the vacancies.

We utilized the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [53, 54] code for our MD simulations. In all simulations a NpT ensemble was used to describe the system. In this ensemble the temperature T, the pressure p and the particle number N, of the system are fixed, while its energy E and volume V are allowed to vary. A Nosé–Hoover thermostat (barostat), as implemented in LAMMPS [54] controlled the system’s temperature (pressure). For each calculation, the simulation cell was first brought into an equilibrium state. Equilibrium was deemed to have been reached when U and V were observed to only fluctuate around constant values. The time required to attain equilibrium varied between 150 ps and 500 ps depending on the number of oxygen defects. As a rule of thumb: the more time was needed, the smaller the number of migrating

### Table 1. Parameters for the empirical pair-potentials used in the simulations.

| Pair | A / eV | ρ / Å | C / eVÅ⁶ | Reference | Usage |
|------|--------|-------|-----------|-----------|-------|
| Ce⁴⁺—O²⁻ | 1 986.83 | 0.351 | 20.40 | [44] | defect calculations CeO₂ |
| Ce³⁺—O²⁻ | 1 731.62 | 0.364 | 14.43 | [44] | defect calculations CeO₂ |
| O²⁻—O²⁻ | 22 764.30 | 0.149 | 27.89 | [45] | defect calculations UO₂ |
| Nb³⁺—O²⁻ | 1 425.00 | 0.365 | 0.00 | [46] | material properties LiNbO₃ |
| Ta⁵⁺—O²⁻ | 1 315.00 | 0.369 | 0.00 | [47] | defect calculations KTaO₃ |
| Gd³⁺—O²⁻ | 1 336.8 | 0.355 | 1.00 | [48] | dopants for binary oxides |

* The short-range potential cutoffs were set at 15 Å.
particles. After equilibration, the simulation was run for 1.4 ns to produce transport data. The software package OVITO [55] was used to visualize the simulation results.

3. Results and discussion

3.1. Oxygen-interstitial and oxygen-vacancy in CeO₂

The same three-step procedure was used to determine the defect diffusivity, regardless of whether the results were obtained from oxygen-deficient or oxygen-excess simulation cells. First, we computed from the appropriate MD simulation the mean-squared-displacement of the oxygen ions, \( \langle r_{O}^2 \rangle \), as a function of time \( t \). Such data are shown in figure 1 for a defect site fraction of 0.91%, for the two different defect species at various temperatures. In both cases, \( \langle r_{O}^2 \rangle \) increases linearly with time, indicating that diffusion took place. Second, we applied the standard Einstein relation,

\[
\frac{d\langle r_{O}^2 \rangle}{dt} = 6D_{O}^{i}
\]

(1)

to these data to obtain the tracer diffusion coefficients of oxygen, \( D_{O}^i \). It is worth noting that even without calculating exact values of \( D_{O}^i \) one recognises that, at \( T = 2000 \) K for example, \( \langle r_{O}^2 \rangle \) is much higher for oxygen-deficient than for oxygen-excess cells. This is a qualitative indication that vacancies are more mobile than interstitials. Third, knowing the defect site fraction \( n_{i/v} \) and the tracer correlation factor \( f_{i/v}^* \) for the two oxygen defects, we extracted the respective defect diffusivity,

\[
D_{i/v} = \frac{D_{O}^i}{f_{i/v}^* n_{i/v}}.
\]

(2)

\( f^* \) depends on the migration mechanism and the symmetry of the sublattice on which diffusion takes place. For the fluorite structure, migration of anion interstitials can either occur by an interstitial mechanism or by a non-colinear interstitialcy mechanism. All our MD simulations confirmed that the trajectories of the anions were consistent with the second possibility. For the interstitials, we thus have \( f_{i}^* = 0.98 \) [56–58], while for the vacancies we have \( f_{v}^* = 0.65 \) [56, 58, 59]. Defect site fractions of oxygen interstitials and oxygen vacancies ranged, as noted previously, from ca.0.1% to 1.8%; the obtained defect-diffusivity data are shown in figure 2.

Comparing \( D_i \) with \( D_v \), for a given temperature \( T \) and defect site fraction \( n_{i/v} \), we see that the vacancy diffusivity is always higher than interstitial diffusivity. For low \( n_{i/v} \), both isothermal values of \( D_i \) and \( D_v \) are constant, albeit with different values. With increasing \( n_{i/v} \) the defect diffusivities start to deviate from the values obtained for low \( n_{i/v} \). \( D_i \) decreases with increasing \( n_{i/v} \) whereas \( D_v \) increases with increasing \( n_i \). Since no other defects are present in these bcc simulation cells, these deviations can be attributed to defect–defect self-interactions. For both defect species the deviations from the regions of constant diffusivity values begin at roughly \( n_{i/v} \approx 1\% \). Hence, for \( n_{i/v} > 1\% \), oxygen point-defects should not be treated as a dilute solution, as far as diffusion is concerned, but rather as a concentrated solution.

Assuming, for simplicity, that the defects execute a random walk in three dimensions, one can express the defect diffusivity in terms of the jump distance \( d_{i/v} \); the number of possible lattice sites to which the defect can
jump, $Z_i$; the attempt frequency $\nu_0$, and the activation entropy $\Delta S_{\text{mig}}$ and activation enthalpy $\Delta H_{\text{mig}}$ of migration [13, 60, 61].

$$D(T) = \frac{d_{jv}^2 Z_i \nu_0}{6} e^{\frac{\Delta S_{\text{mig}}}{k_B}} e^{\frac{\Delta H_{\text{mig}}}{k_B}}$$

(3)

For interstitialcy migration, $Z_i = 8$ and $d_i = a(T) \sqrt{3}/4$, where $a(T)$ is the lattice parameter taken from the MD simulation at temperature $T$. For vacancy migration, $Z_v = 6$ and $d_v = a(T)/2$. Assuming a common $\nu_0$ value (of $10^{13}$ s$^{-1}$) for both interstitialcy and vacancy migration, we find, by applying equation (3) to the data in figure 2, the values of $\Delta H_{\text{mig,i}}$ and $\Delta S_{\text{mig,i}}$ plotted in figures 3(a) and (b) against their corresponding defect site fractions.

The activation enthalpy of interstitialcy migration is found to be $\Delta H_{\text{mig,i}} = (1.40 \pm 0.05)$ eV for low $n_i$; for $n_i > 1\%$, it decreases. In comparison, the activation enthalpy of vacancy migration is much lower, at $\Delta H_{\text{mig,v}} = (0.63 \pm 0.02)$ eV, and it rises with increasing $n_v$. When considering the activation entropies, we restrict our comments to the results obtained for the dilute solutions, since the values for concentrated solutions are effective values, modified by defect–defect interactions. We find, as expected, values of the order of several $k_B$, with a positive value of $\Delta S_{\text{mig,i}} = +(0.73 \pm 0.25) k_B$ and a negative value of $\Delta S_{\text{mig,v}} = (-0.84 \pm 0.07) k_B$. Curiously, the absolute magnitude of the activation entropy is nearly the same in both cases. It is unclear at present whether this is simply coincidence.
Interstitial diffusivity $D_i$ against inverse temperature. (a) Comparison of results for an 0.9% NbCe$_{0.9}%$-doped cell ([A] blue circles) and for the bgcc cell ([B] red squares) with the same oxygen interstitial content ($n_i = 0.45\%$); (b) Comparison of results for charge compensation of Nb by O$_i^-$ ([A] blue circles) and for charge compensation by 0.09% O$_b^-$ and 0.72% CeCe$_{0.72}\%$ [C] black triangles); (c) Comparison of results for two different donor dopants TaCe$_{0.9}\%$ ([D] orange diamonds) and NbCe$_{0.9}\%$ ([A] blue circles), both cells with a dopant content of 0.9% and a corresponding oxygen interstitial content of 0.45%.

3.2. Oxygen-interstitial diffusion in donor-doped CeO$_2$

In figure 4 we compare the results for our NbCe$_{0.9}\%$-doped cell with the undoped cell and two differently doped cells. The first case, figure 4(a), compares the values for $D_i$ of the bgcc cell (with $n_i = 0.45\%$), with values from a cell containing the same site fraction of oxygen interstitials, but also containing NbCe$_{0.9}\%$, such that the charge of the interstitials is exactly compensated by the charge of the dopant. There is a significant difference between the two cases, with $D_i$ in the NbCe$_{0.9}\%$-doped cell being higher and exhibiting a smaller activation enthalpy of interstitial migration, $\Delta H_{mig,i} = (1.22 \pm 0.04)$ eV, compared with $\Delta H_{mig,i} = (1.42 \pm 0.03)$ eV for the undoped cell. These results clearly show that NbCe$_{0.9}\%$ has a beneficial effect on the diffusion of oxygen interstitials.

In the second case (figure 4(b)) both cells contained a site fraction of 0.9% NbCe$_{0.9}\%$ ions, but in the one case the dopants were charge-compensated only by oxygen interstitials and in the second case they were compensated mostly by CeCe$_{0.72}\%$ with only a few O$_b^-$ ions. The reason for this comparison is that, according to defect chemical modelling, NbCe$_{0.9}\%$ as a donor dopant is compensated primarily by CeCe$_{0.72}\%$ for a wide range of conditions. Here, both sets of MD simulations indicate similar interstitial diffusion coefficients. The data for the second set display more scatter, and this is due to the low number of oxygen interstitials. The activation enthalpy of interstitial migration for this case is $\Delta H_{mig} = (1.08 \pm 0.12)$ eV, with the large error coming from the poor statistics, but it is comparable to the data for the cell containing only O$_i^-$ to compensate NbCe$_{0.9}\%$, $\Delta H_{mig} = (1.22 \pm 0.04)$ eV. As the CeCe$_{0.72}\%$ ions do not seem to influence the diffusion of oxygen interstitials, we will not consider CeCe$_{0.72}\%$ in the following simulations and therefore only focus on donor dopants and oxygen interstitials.

In the third case (figure 4(c)) the results for the two different donor dopants (NbCe$_{0.9}\%$ and TaCe$_{0.9}\%$) are compared. Both simulation sets show very close agreement for the absolute values for $D_i$, and the activation enthalpies of interstitial migration are similar, too: $\Delta H_{mig} = (1.23 \pm 0.04)$ eV for the Nb-doped cell and $\Delta H_{mig} = (1.22 \pm 0.03)$ eV for the Ta-doped one. Evidently, it does not matter which of these two pentavalent dopants is used, as they both yield essentially the same results, at least according to these simulations.

Given the positive effect of Nb on the interstitial diffusivity, we performed MD simulations of oxygen-interstitial diffusion as a function of Nb content, with the donors’ charge being compensated exactly by the interstitials’ charge. For each concentration three simulations were conducted to enhance the quality of the statistics. The results are plotted in figure 5(a). There is a clear trend of $D_i$ increasing and $\Delta H_{mig}$ decreasing with increasing Nb concentration. Defect–defect interactions between oxygen interstitials can be excluded as the sole reason for this behaviour, as the deviation in the bgcc cells was smaller (see figure 2(a)) and the activation enthalpy of interstitial migration was unaffected for the dilute solution case, opposed to the behaviour shown in figure 5(a).

Figure 5(b) shows the activation enthalpy of interstitial diffusion obtained from the simulations plotted against the mean Nb–Nb spacing. With a decrease in the mean Nb–Nb spacing the migration enthalpy...
decreases, too. Or to rephrase it, with increasing NbCe site fraction the activation enthalpy of interstitial migration decreases. The difference in the activation enthalpy of interstitial diffusion for the cells with the lowest and with the highest mean spacing amounts to roughly 0.4 eV, which is quite significant.

Figure 6. Oxygen-ion trajectories (in orange) for interstitial diffusion in (a) the bgcc cell, with $n_i = 0.46\%$ and (b) NbCe-doped cell, with $n_i = 0.46\%$ and $n_{Nb} = 0.91\%$. Nb dopants are shown in green. In both cases the mean-squared-displacement of the oxygen ions was the same.

Figure 5. (a) Oxygen-interstitial diffusivity $D_i$ against inverse temperature for varying site fractions of NbCe (0.36\% to 3.6\%) with accompanying oxygen-interstitial site fractions; (b) Activation enthalpy of interstitial migration against the average Nb–Nb distance.

decrees, too. Or to rephrase it, with increasing NbCe site fraction the activation enthalpy of interstitial migration decreases. The difference in the activation enthalpy of interstitial diffusion for the cells with the lowest and with the highest mean spacing amounts to roughly 0.4 eV, which is quite significant.

In figure 6 the oxygen-ion trajectories for the bgcc and the NbCe-doped cell are compared for the same total mean-squared-displacement of all oxygen ions (this ensures that the oxygen ions in both cases have the same number of successful jumps); the site fraction of oxygen interstitials is also the same. In the case of the bgcc simulation cell the oxygen trajectories are homogeneously distributed throughout the cell. For the niobia-doped simulation cell the oxygen trajectories are concentrated around the NbCe ions. The O$_{\text{I}i}$ ions seem to prefer to reside in the close proximity of the NbCe ions and seem to jump mainly around the NbCe ions. If the obtained diffusivity results ($D_i$ and $\Delta H_{\text{mig},i}$) are taken into account, it seems that the oxygen interstitials are more mobile in the proximity of NbCe than in the proximity of CeCe, as most of the jumps are in the neighbourhood of NbCe and the diffusion data for the doped cell indicates faster oxygen diffusion than for the undoped cell.
3.3. Oxygen-vacancy diffusion in acceptor-doped CeO$_2$

For the sake of completeness, we also examine the interactions between dopant cations and mobile defects in cells with oxygen vacancies. It can be seen in figure 7 that the presence of the acceptor-dopant Gd$_{Ce}$ leads to a decrease in the oxygen-vacancy diffusivity and to an increase in the activation enthalpy of vacancy migration, from $\Delta H_{mig,v} \approx 0.62$ eV to $\Delta H_{mig,v} \approx 0.80$ eV.

In figure 8(a) values of $D_v$ for various oxygen-vacancy site fractions are plotted against inverse temperature. In comparison with results for oxygen-vacancy diffusion in the bgcc simulation cell (see figure 2(b)), the presence of Gd$^{3+}$ leads to an overall decrease in diffusivity by a factor of roughly 2, with no further modification beyond the already observed one due to oxygen vacancy-vacancy interactions. The Gd$_{Ce}$ site fraction does not seem to have an effect on the activation enthalpy of vacancy migration, beyond the increase of $\Delta H_{mig,v}$ in comparison to the obtained values for the undoped cell. For all Gd$_{Ce}$ site fractions looked at, the obtained values for $\Delta H_{mig,v}$ seem to fall around $(0.82 \pm 0.05)$ eV, in contrast to activation enthalpies of migration reported by Faber et al [64]. A possible reason for the difference between the reported values by Faber et al and our results is that Gd was randomly distributed in our simulation cells, whereas in the samples of Faber et al, Gd was mobile at the sintering temperature, and thus able to form clusters and nanophases, as predicted by Zguns et al [63].

In figure 9 the oxygen trajectories for the undoped and Gd$_{Ce}$-doped cell, with the same $n_v$ are shown. For the undoped cell (shown in figure 9(a)) the oxygen ions have moved homogeneously through the cell, as indicated...
by the homogeneous distribution of the trajectories. In figure 9(b) the oxygen trajectories for the Gd$^{3+}$-doped cell are shown. The trajectory distribution is less homogeneous than for the undoped cell, indicating an interaction between the dopant and the vacancies. In the proximity of the dopant ions, the trajectory distribution is more dense, indicating more oxygen jumps. The effect is similar to the observation for the Nb$^{3+}$-doped cell, albeit not as pronounced, with the fundamental difference that in the acceptor-doped cells the overall oxygen-vacancy diffusivity is reduced in comparison to the undoped cells. The oxygen-vacancies seem to prefer to reside in the proximity of Gd$^{3+}$, similar to the behaviour of the oxygen-interstitials in the donor-doped case. But in contrast to the behaviour of oxygen-interstitials, here the interaction between the dopant and the vacancies results in a reduced diffusivity.
oxygen vacancy leads to a higher migration barrier and through this to a decrease in the oxygen vacancy diffusivity. The oxygen vacancies are less mobile in the proximity of the dopant ions.

### 3.4. Literature discussion

In figure 10 we compare our computational results with experimental and computational results for dilute solutions of oxygen defects and dopants in CeO$_2$ and other AO$_2$ systems. We take our results for doped cells, since the experimental systems are doped at similar levels. In table 2 we give a comprehensive list of experimentally obtained and theoretically predicted activation enthalpies of migration for both dilute and concentrated systems.

In general, we see in figure 10 that the diffusion coefficients for oxygen vacancies are higher than those for oxygen interstitials for all fluorite-structured oxides. The temperature dependence of the defect diffusivity is stronger for oxygen interstitials than for oxygen vacancies, that is, the activation enthalpy of migration is higher for oxygen interstitials than for oxygen vacancies.

Comparing our predicted $D_i$ values with reported values for oxygen-interstitial diffusion in CeO$_2$ and two other AO$_2$ oxides (UO$_2$, PuO$_2$), we find all of them to be of comparable order of magnitude. In particular, we find a good agreement between the experimentally found values for Ce$_{0.999}$Nb$_{0.001}$O$_{2+\delta}$ [62] and Ce$_{0.999}$U$_{0.001}$O$_{2+\delta}$ [65] and our data for Ce$_{0.98}$Nb$_{0.01}$O$_{2+\delta}$ extrapolated down to the temperatures of experiment.

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**Table 2.** Comparison of defect migration enthalpies for CeO$_2$ and other various AO$_2$-type oxides.

| Material | $\Delta H_{\text{mag}}$ | Study |
|----------|----------------|-------|
| CeO$_2$  | 1.42 ± 0.02 (O$_{\text{i}}^+$) | This study |
| CeO$_2$  | 0.63 ± 0.02 (V$_{\text{o}}^-$) | This study |
| 1% Gd:CeO$_2$ | 0.76 ± 0.03 (V$_{\text{o}}^-$) | This study |
| 1% Nb:CeO$_2$ | 1.22 ± 0.04 (O$_{\text{i}}^+$) | This study |
|          | 1.28 ± 0.13 (O$_{\text{i}}^+$) | [62] |
| 0.1% U:CeO$_2$ | 1.23 ± 0.03 (O$_{\text{i}}^+$) | [65] |
| 5% U:CeO$_2$ | 1.42 ± 0.14 (O$_{\text{i}}^+$) | [65] |
| CeO$_2$  | 0.80 (O$_{\text{i}}^+$) | [37] |
|          | 0.73 (V$_{\text{o}}^-$) | [64] |
|          | 0.72 (V$_{\text{o}}^-$) | [73] |
|          | 0.5 (V$_{\text{o}}^-$) | [28] |
|          | 0.5 (V$_{\text{o}}^-$) | [23] |
|          | 0.62 (V$_{\text{o}}^-$) | [26] |
|          | 0.47 (V$_{\text{o}}^-$) | [46] |
|          | 0.51 (V$_{\text{o}}^-$) | [27] |
|          | 0.6 (V$_{\text{o}}^-$) | [32] |
|          | 0.47 (V$_{\text{o}}^-$) | [33] |
|          | 0.57 (V$_{\text{o}}^-$) | [31] |
|          | 0.52 (V$_{\text{o}}^-$) | [74] |
|          | 0.6 (V$_{\text{o}}^-$) | [75] |
|          | 0.9 (V$_{\text{o}}^-$) | [76] |
|          | 1.1 (V$_{\text{o}}^-$) | [77] |
| Ta$_x$CeO$_2$ | 0.25 ± 0.05 (O$_{\text{i}}^+$) (NMR) | [43] |
| UO$_2$   | 1.00 (O$_{\text{i}}^+$) | [39] |
|          | 1.11 (O$_{\text{i}}^+$) | [67] |
|          | 0.67 (V$_{\text{o}}^-$), 0.93 (O$_{\text{i}}^+$) calc. | [25] |
|          | 0.75 ± 0.08 exp. | [25] |
|          | 0.54 (V$_{\text{o}}^-$), 0.64 (O$_{\text{i}}^+$) calc. | [41] |
|          | 0.51 (V$_{\text{o}}^-$), 1.0 (O$_{\text{i}}^+$) exp. | [41] |
| PuO$_2$  | 1.11 (V$_{\text{o}}^-$), 1.18 (O$_{\text{i}}^+$) calc | [66] |
|          | 0.62 (V$_{\text{o}}^-$), 1.04 (O$_{\text{i}}^+$) exp | [66] |
|          | 0.48 (V$_{\text{o}}^-$), 1.58 (O$_{\text{i}}^+$) exp | [41] |
| m-HfO$_2$ | 0.5 (V$_{\text{o}}^-$) | [68] |
|          | 0.66 (V$_{\text{o}}^-$) | [71] |
|          | 1.8 (O$_{\text{i}}^+$) | [42] |
| c-HfO$_2$ | 0.43 (V$_{\text{o}}^-$) | [71] |
| ThO$_2$  | 1.04 (O$_{\text{i}}^+$) | [37] |
|          | 0.78 (V$_{\text{o}}^-$), 0.92 (O$_{\text{i}}^+$) calc. | [41] |
The activation enthalpy of interstitial migration $\Delta H_{mig,i}$ in AO$_2$ oxides lies in the range of $\Delta H_{mig,i} = (0.9$ to $1.3)$ eV [25, 39, 65–67], to which our results fit well. Again the agreement between the result of the simulation (containing Nb$^{5+}$) $\Delta H_{mig,i} = (1.22 \pm 0.04)$ eV and the experimental results for [Ce$_{0.99}$Nb$_{0.01}$O$_2$ $+$ $\delta$] $\Delta H_{mig,i} = (1.28 \pm 0.13)$ eV [62] and [Ce$_{0.999}$U$_{0.001}$O$_2$ $+$ $\delta$] $\Delta H_{mig,i} = (1.22 \pm 0.03)$ eV [65] is extremely good.

Regarding oxygen-vacancy diffusion, our predicted values for $D_v$ seem to be an underestimation, in comparison with results for [Ce$_{0.99}$Gd$_{0.01}$O$_1.995$] [64], but show surprisingly good agreement with values for m-HFO$_{1.9875}$, UO$_{2-\delta}$ and PuO$_{2-\delta}$. Generally the activation enthalpy of oxygen-vacancy migration in AO$_2$ materials seems to lie in the range of 0.5 eV to 0.8 eV, which is in good agreement with our results, $\Delta H_{mig,v} = (0.63 \pm 0.02)$ eV for the bcc cell and $\Delta H_{mig,v} = (0.76 \pm 0.03)$ eV for the cell with $n_{Gd} = 0.91\%$.

Let us now extend the scope of our considerations to the migration of anion vacancies and anion interstitials in the original fluorites, BaF$_2$ and CaF$_2$. Guo and Maier [72] in their detailed analysis found for the migration of fluorine-vacancies and fluorine-interstitials values of $\Delta H_{mig,v} = 0.56$ eV and $\Delta H_{mig,i} = 0.79$ eV for BaF$_2$ and $\Delta H_{mig,v} = 0.51$ eV and $\Delta H_{mig,i} = 0.92$ eV for CaF$_2$. Similar to the oxygen migration in AO$_2$ the activation enthalpy of vacancy migration is lower than the activation enthalpy of interstitial migration.

The reason for such behaviour, we propose, is rooted in the crystal structure. The vacancy mechanism does not require the migrating ion to come into direct contact with other anions, whereas the interstitialcy mechanism specifically requires this. Comparing the activation enthalpies of vacancy migration for AO$_2$ and A$'$F$_2$ materials, we recognise that the fluorine diffusion in A$'$F$_2$ has a lower migration enthalpy than oxygen diffusion in AO$_2$, and the same holds true for the diffusion of interstitials. The reason for this could be that the migration of single charged F$^-$ is less hindered than the migration of the double charged O$^{2-}$. Genreith-Schriever et al [28] examined using computational methods the migration behaviour of various anions in CeO$_2$, and found that a higher negative charge on the migrating ion leads to a higher migration barrier. This would support our explanation for the observed difference between the F$^-$ and the O$^{2-}$ migration. 3.5. Conclusions

(i) At a given temperature and defect site fraction, oxygen vacancies were found to exhibit a higher diffusivity than oxygen interstitials in CeO$_2$, $D_v > D_i$.

(ii) For dilute defect concentrations ($n_{i/v} \leq 0.91\%$), the activation enthalpy of vacancy migration was substantially lower than that of interstitial migration, $\Delta H_{mig,v} < \Delta H_{mig,i}$.

(iii) Defect–defect self-interactions are different in nature for vacancies and interstitials. Going beyond the dilute limit leads to $D_i$ increasing but $D_v$ decreasing. This is accompanied by $\Delta H_{mig,i}$ decreasing, but $\Delta H_{mig,v}$ increasing.

(iv) The fundamental difference between oxygen-vacancy and oxygen-interstitial migration in fluorite-structured materials is attributed to the crystal structure.

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