The Effect of Jump Attempt Frequencies on the Ionic Conductivity of Doped Ceria

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Abstract

The macroscopic oxygen ion conductivity in doped ceria is determined by the microscopic activation energy barriers and jump attempt frequencies of oxygen ion jumps. While the influence of the local jump environment on the migration energy is widely investigated, its influence on the attempt frequency is rarely investigated. In this work, attempt frequencies in Sm, Yb and Gd doped ceria are calculated using density functional theory. Moreover, ionic conductivities for varying local jump attempt frequencies in different jump environments are investigated using Kinetic Monte Carlo simulations. For doping along the migration pathway, where the migrating oxygen ion passes between two adjacent cations, large dopants lead to an increase and small dopants to a decrease in the attempt frequency. Sm doping in nearest neighborhood to the start position of the migrating oxygen vacancy also leads to an increase in attempt frequency. Kinetic Monte Carlo simulations show that at intermediate Sm dopant fractions oxygen vacancies frequently jump towards and away from dopants explaining why Sm doped ceria has one of the highest conductivities reported for a ternary cerium oxide due to its low dopant-oxygen vacancy association in both nearest and next-nearest neighborhood.

Introduction

The ionic conductivity is a key property for applications including Solid Oxide Fuel Cells and Solid Oxide Electrolyzer Cells for energy storage,^{1,2} oxygen sensors similar to the lambda sensor in cars, which controls the combustion of fuel,³ as well as oxygen membranes.⁴⁻⁷ For a better understanding, oxygen ion conductivities have been calculated in the commonly used material rare-earth doped ceria using analytical models,⁸⁻¹² Molecular Dynamics (MD) simulations,¹³⁻¹⁸ and Kinetic Monte Carlo (KMC) simulations.¹⁹⁻²⁹

Ab initio based ionic conductivities were especially calculated using KMC simulations with parameters that were obtained from density functional theory (DFT).²³⁻²⁹ Instead of propagating the classical equations of motions forward in time and simulating atomic vibrations in time steps of about 10^{-15} s, which is done in MD, KMC simulations use the knowledge that systems typically evolve with time through diffusive jumps from state to state.^{19,30,31} These occasional jumps shall be limited by an energy barrier $E_{\text{mig},p}$, which has to be surmounted by the system for each pathway of an oxygen ion p. As the transition rate $\Gamma_p = \nu_{0,p} \cdot e^{-\frac{\Delta E_{\text{mig},p}}{k_B T}}$ with the attempt frequency $\nu_{0,p}$ depends only on the initial and transition state according to the transition state theory,³²⁻³⁴ the KMC method is a Markov process.

The attempt frequency $\nu_{0,p}$ depends on the temperature T, the vibrational energy difference $\Delta E_{\text{vib},p}$, and, in particular, the vibrational entropy difference $\Delta S_{\text{vib},p}$ between initial and transition state.³⁴ In literature, only few studies calculated the attempt frequency in doped ceria. Dholabhai *et al.* calculated the attempt frequency for praseodymium doped ceria by means of density functional theory with a Hubbard U parameter (DFT+U) resulting in $5 \cdot 10^{12} \text{ s}^{-1}$ for one of many possible ionic configurations.²³ However, only the Gamma point phonons were considered. Attempt frequencies for different ionic configurations are rarely calculated. Tarancón *et al.* used classical MD to indirectly calculate attempt frequencies for Ce_{0.92}Gd_{0.08}O_{1.96} resulting in $(5.4 \pm 0.3) \cdot 10^{12} \text{ s}^{-1}$ for jumps through an edge formed both by two host cations (Ce-Ce edge, see Fig. 1) or one dopant and one host cation (Ce-Gd edge).¹⁶

For Kinetic Monte Carlo simulations, the migration energies and the attempt frequencies must be known for all occurring jump configurations containing multiple dopants and oxygen vacancies at various positions. The attempt frequency is often assumed to be a constant estimated value for all occurring jumps in the doped system.²³ However, attempt frequencies can easily differ between jump configurations by a factor of three as shown in our earlier publication for Sm doped ceria.³⁴ In this work, we will extend our work to further jump configurations as well as to Yb and Gd doped ceria. Moreover, we will show the effect of the jump attempt frequencies on the ionic conductivity in doped ceria. Understanding the effect of the jump attempt frequency on the ionic conductivity provides an important contribution to the future development of sustainable and efficient materials.

The paper is organized as follows: In section 2, we discuss the oxygen diffusion in ceria, the transition state theory according to Eyring and Vineyard and the attempt frequency in pure and Sm doped ceria for doping at the migration edge. In section 3, computational details according to the general computational setup and the phonon calculations are described. In section 4, we present our results for the attempt frequencies in Sm, Yb and Gd ceria. Finally, we show the influence of varying local jump attempt frequencies on the ionic conductivity. In section 5, we give a short summary.

Theory

Ceria (CeO₂) has the fluorite structure $(Fm\bar{3}m)$ for temperatures between room temperature and the melting point.^{35–37} The cations are positioned in a face-centered cubic lattice while the anions fill the tetrahedral holes leading to a primitive cubic anion lattice. Oxygen vacancies lead to ionic conductivity as oxygen ions can jump to a vacant lattice site (hopping mechanism). For the oxygen ion conductivity, jumps of oxygen ions or vacancies occur mainly between adjacent tetrahedral oxygen sites in (100) direction³⁸ with the experimental jump distance *l* given by half of the unit cell length at room temperature.³⁶ Along the migration pathway, the migrating oxygen ion passes between two adjacent cations, which form a "migration edge" as shown in Fig. 1.^{27,39}

In doped ceria, defects are predominantly created by doping.⁴⁰ In this work, cerium oxide CeO_2 is doped with lower valent rare-earth oxides RE_2O_3 . This leads to the creation of oxygen vacancies as shown in Eq. 1 in Kröger-Vink notation.³⁶

$$\operatorname{RE}_2\operatorname{O}_3 \longrightarrow 2\operatorname{RE}'_{\operatorname{Ce}} + 3\operatorname{O}_{\operatorname{O}}^{\times} + \operatorname{V}_{\operatorname{O}}^{\bullet\bullet} \tag{1}$$

As a result, oxygen vacancies are the majority defects with a concentration controlled by the dopant fraction according to $\left[\operatorname{RE}'_{\operatorname{Ce}}\right] = 2\left[\operatorname{V}^{\bullet\bullet}_{\operatorname{O}}\right]$. Doping is limited by solubility. For Sm, Yb and Gd doped ceria, large solubilities above x = 0.3 have been reported, ^{41–45} It is known that under oxygen-poor conditions ceria can be reduced leading to the formation of polarons ^{46,47}



Figure 1: Possible migration edge configurations in samarium doped ceria. Ce-Ce edge (left), Ce-Sm edge (middle) and Sm-Sm edge (right). Cerium ions (green), samarium ions (blue), oxygen ions (red spheres) and oxygen vacancies (red boxes).²⁷ - Reproduced by permission of the PCCP Owner Societies

and a number of theoretical studies have been dedicated to this subject.^{48–54} However, we restrict our simulations to conditions were the electronic conductivity is significantly smaller than the ionic conductivity and thus can be neglected.

For better clarity, we consider at first only one out of all possible jump processes shown e.g. in Fig. 1. The transition rate and the attempt frequency for this process are given by the transition state theory according to Eyring³² and Vineyard.³³ The Eyring formula for the jump rate at constant volume (Eq. 2) is obtained by assuming a quasi-equilibrium between the initial state (IS) and transition state (TS):^{32,34}

$$\Gamma(V,T) = \underbrace{\frac{k_{\rm B}T}{h} e^{\frac{\Delta S_{\rm vib}(V,T)}{k_{\rm B}}} e^{-\frac{\Delta E_{\rm vib}(V,T)}{k_{\rm B}T}}_{\nu_0(V,T)} e^{-\frac{\Delta E_{\rm el}^0(V)}{k_{\rm B}T}} (2)$$

where $\Delta E_{\rm el}^0$ is the electronic energy difference, $\Delta E_{\rm vib}$ is the vibrational energy difference and $\Delta S_{\rm vib}$ the entropy difference of initial and transition state, T is the absolute temperature, V is the cell volume, $k_{\rm B}$ is the Boltzmann constant and h is the Planck constant. The transition rate in Eq. 2 is a product of an attempt frequency, here $\nu_0(V,T)$, and an exponential term containing the electronic energy difference, $\Delta E_{\rm el}^0(V)$. The definition of the attempt frequency according to Eyring in Eq. 2 is commonly used in literature. In general, $\nu_0(V,T)$ is independent of temperature at high temperatures.^{34,55,56} The electronic energy difference $\Delta E_{\rm el}^0$ is obtained from *ab initio* DFT calculations at T = 0 K and is, thus, independent of temperature.

Vineyard adapted Eyring's concept in the approximation of high temperatures and for vibrational frequencies of atoms that are, however, calculated only at the Gamma point. As shown in our earlier work, Vineyard's formula can be adapted to include lattice vibrations that are calculated for any phonon mesh:³⁴

$$\nu_{0} = \frac{\prod_{q=1}^{M} \prod_{i=1}^{N} \nu_{q,i}^{\frac{1}{M}}}{\prod_{m=1}^{M} \prod_{j=1}^{N-1} \nu_{m,j}^{\frac{1}{M}}}.$$
(3)

where $\nu_{q,i}$ and $\nu_{m,j}$ are the normal frequencies of lattice vibrations in the initial state (nominator in Eq. 3) and transition state (denominator in Eq. 3) for M discrete wave vectors with the indexes q and m. Here, the N or N-1 phonon bands, equivalent to the degrees of freedom, have the indexes i and j for the initial and transition state, respectively. If only the Gamma point is considered (M = 1), the classical Vineyard formula is obtained.

All phonon calculations in this work are performed for a constant volume that was derived for bulk ceria at the absolute zero. The isobaric behavior can be investigated at a pressure of p = 0 by determining the minimum of the free energy for different volumes at given temperatures. Due to the high computational demand of phonon calculations, it is commonly assumed that the change in vibrational entropy with volume, $\left(\frac{\partial S_{\text{vib}}}{\partial V}\right)_T$, is identical for the defect-free bulk, the defective cell in the initial state, and the defective cell in the transition state as well.^{57,58} Then, the entropy of migration is given according to:⁵³

$$\Delta S_{\text{vib}}(p,T) = \Delta S_{\text{vib}}(V(p,T),T)$$

$$= \Delta S_{\text{vib}}(V_0,T) + \int_{V_{\text{IS}}(p,T)}^{V_{\text{IS}}(p,T)+\Delta V} \left(\frac{\partial S_{\text{vib}}}{\partial V}\right)_T^{\text{bulk}} dV$$

$$= \Delta S_{\text{vib}}(V_0,T) + \alpha_V B_T \cdot \Delta V, \qquad (4)$$

with the equilibrium volume V_0 , the volumetric thermal expansion coefficient α_V , the bulk modulus B_T , the change in volume between the transition state and initial state at constant pressure $\Delta V = V_{\text{TS}} (p = 0, T) - V_{\text{IS}} (p = 0, T)$, which is assumed to be independent of temperature.

Therewith, the Eyring formula (Eq. 2) can be easily modified to investigate isobaric be-

havior. Subsequently, the Eyring formula can again be approximated for high temperatures. This results into a modified form of the generalized Vineyard result (Eq. 3):⁵⁹

$$\nu_0(p) = \frac{\prod_{q,i} \nu_{q,i}^{\frac{1}{M}}}{\prod_{m,j} \nu_{m,j}^{\frac{1}{M}}} \exp\left(\frac{\alpha_{\rm V} B_{\rm T} \Delta V}{k_{\rm B}}\right).$$
(5)

In our earlier work, the attempt frequency for an oxygen ion jump in pure ceria and Sm doping at the migration edge was calculated.³⁴ Convergence checks of the phonon mesh revealed that the common reduction to the Gamma point is not sufficient to calculate the attempt frequency. Calculations of Sm doped ceria revealed an unchanged attempt frequency for jumps through a Ce-Sm edge due to a curved oxygen migration path (Table 1). However, for jumps through a Sm-Sm edge, an increase of the attempt frequency was found. Also, a linear correlation between the migration energies $\Delta E_{\rm el}^0$ and the difference of the distances of the edge cations between the transition and initial state, $d_{\rm TS} - d_{\rm IS}$, was found. For larger widening of the edge cations, larger migration energies are found. Similarly, the attempt frequency correlates with the edge cation distance in the transition state $d_{\rm TS}$. For the Ce-Ce and Ce-Sm edge ν_0 and $d_{\rm TS}$ are similar, respectively. However, both values increase significantly for the Sm-Sm edge.

Table 1: Electronic migration energies for different migration configurations (Eq. 2), distances of the edge cations in the initial and the transition state and attempt frequencies $\nu_0 (V, T)$ for an oxygen-vacancy exchange process (Vineyard, Eq. 3) at constant volume (V = const.).³⁴ - Reproduced by permission of the PCCP Owner Societies

migration	d_{IS}	$d_{\rm TS}$	$d_{\rm TS} - d_{\rm IS}$	$\Delta E_{\mathrm{el}}^{0}\left(V,T\right)$	$\nu_0(V,T)$
edge	(Å)	(Å)	(Å)	(eV)	(s^{-1})
Ce-Ce	4.148	4.267	0.119	0.587	$1.47 \cdot 10^{12}$
Ce-Sm	4.142	4.268	0.126	0.759	$1.49 \cdot 10^{12}$
$\operatorname{Sm-Sm}$	4.141	4.280	0.139	1.166	$4.30\cdot 10^{12}$

For the constant pressure case (p = 0), the hydrostatic pressure in the constant volume case, which is caused by the defect creation compared to the defect-free cell, results in a volume compression for the Ce-Ce, Ce-Sm edge and an expansion for the Sm-Sm edge for

Table 2: Electronic migration energies for different migration configurations, changes in volume between transition state and initial state ΔV and oxygen vacancy attempt frequencies $\nu_0(p,T)$ (Vineyard) at constant pressure (p=0) and 900 K.³⁴ - Reproduced by permission of the PCCP Owner Societies

$\operatorname{migration}$	$\Delta E_{\mathrm{el}}^{0}\left(p,T\right)$	ΔV	$ u_0\left(p,T ight)$
edge	(eV)	$(Å^3)$	(s^{-1})
Ce-Ce	0.602	3.06	$7.67 \cdot 10^{12}$
Ce-Sm	0.769	3.01	$7.52 \cdot 10^{12}$
$\operatorname{Sm-Sm}$	1.162	2.64	$1.79 \cdot 10^{13}$

initial and transition state. As a result, the volume change between the transition state and initial state ΔV is similar for the Ce-Ce and Ce-Sm edge and slightly smaller for the Sm-Sm edge (see Table 2). The attempt frequency increases compared to the constant volume case.

The calculated attempt frequencies are in the range of the usually assumed values $(10^{12} - 10^{13} \text{ s}^{-1})$ and similar to experimental Debye frequencies in pure, Sm and Yb doped ceria, which are between $8 \cdot 10^{12}$ and $10 \cdot 10^{12} \text{ s}^{-1}$ according to ultrasonic pulse, specific heat and thermal expansion coefficient measurements.⁶⁰⁻⁶³

The ionic conductivity σ_i of oxygen ions $(i = O^{2^-})$ or vacancies $(i = V_0^{\bullet\bullet})$ is proportional to their squared charge $z_i^2 e^2$, concentration n_i and mechanical mobility b_i (Eq. 6). For noninteracting defects, the mobility is related to the diffusion coefficient D_i by the classical Einstein relation with the Boltzmann constant $k_{\rm B}$ and the absolute temperature T. Though this approximation fails for most doped materials, it is often used to analyze experimental results. Both diffusion coefficients ($D_{O^{2-}}$ and $D_{V_0^{\bullet\bullet}}$) depend on the weighted mean jump rate of all oxygen ions ($\overline{\Gamma}_{O^{2-}}$) or vacancies ($\overline{\Gamma}_{V_0^{\bullet\bullet}}$) to one nearest neighbor site. In this work, jumps to other lattice sites are neglected according to Nakayama and Martin.³⁸ In Eq. 6, l is the jump distance and γ is the geometrical factor, which includes the number of jump sites $n_{\rm p}$ and the dimension of diffusion d and is $\gamma = \frac{n_{\rm p}}{2d} = 1$ in a primitive cubic lattice, e.g. the oxygen sublattice in ceria.^{55,64} The jump rate can be described by an Arrhenius equation (Eq. 7) with the apparent activation enthalpy $\Delta H_{\rm a}$. The apparent activation enthalpy describes the experimentally determined dependence of the diffusion coefficient on temperature and can be calculated from the slope of a plot $\ln \overline{\Gamma}_i$ versus 1/T.

$$\sigma_i = n_i \cdot z_i^2 e^2 \cdot b_i$$
, where $b_i = \frac{D_i}{k_{\rm B}T}$ and $D_i = \gamma l^2 \cdot \overline{\Gamma}_i$. (6)

$$\overline{\Gamma}_{i} = \overline{\nu}_{\exp,i} \cdot e^{-\frac{\Delta H_{a}}{k_{\rm B}T}} \tag{7}$$

Therefore, the pre-exponential factor for diffusion $D_{0,i} = \gamma l^2 \cdot \overline{\nu}_{\exp,i}$ depends on the mean experimental attempt frequency $\overline{\nu}_{\exp,i}$, which was already discussed in detail in our earlier publication.³⁴ Naturally, deviations in the activation enthalpy, which appears in the exponential term, possess a stronger influence on the jump rate than deviations in the attempt frequency.

As a result, the activation enthalpy can be extracted from the conductivity according to

$$\sigma_i = \frac{A}{T} e^{-\frac{\Delta H_a}{k_{\rm B}T}} \tag{8}$$

with the parameter A. In doped ceria, a variety of ionic configurations occurs, which leads to a variety of jump environments and possibly different local attempt frequencies. The extracted activation enthalpy $\Delta H_{\rm a}$ is therefore a macroscopic property influenced by all jumps.

Computational details

All calculations were performed by means of density functional theory within the generalized gradient approximation (GGA) according to Perdew, Burke and Ernzerhof⁶⁵ (PBE) and the projector augmented-wave method⁶⁶ (PAW) using the Vienna Ab initio Simulation Package (VASP).^{67,68} Plane waves with an energy cutoff of 500 eV and a $2 \times 2 \times 2$ Monkhorst-Pack k-point mesh for the simulation cell constructed from 16 unit cells were applied according to earlier publications.^{28,34,53} The convergence parameters for electronic and ionic relaxation were set to 10^{-8} eV and 10^{-4} eV/Å, respectively, to guarantee a sufficient accuracy of the calculated forces. The $5s^25p^66s^25d^14f^1$ electrons of the cerium atoms, the $5s^25p^66s^25d^1$ elec-

trons of the samarium atoms, the $5p^{6}6s^{2}5d^{1}$ electrons of the gadolinium atoms, the $5p^{6}6s^{2}$ electrons of the ytterbium atoms and the $2s^22p^4$ electrons of the oxygen atoms were treated as valence electrons. A Hubbard U parameter was introduced to account for the localization of strongly correlated electrons by the rotational invariant approach.⁶⁹ A value of 5 eV for the 4f-orbitals of cerium was chosen according to earlier studies.^{25,70–77} For all defective cells, the total number of electrons in the cell was adapted to reproduce the actual charge state of the different defects, e.g. $(Ce_{64}O_{127})^{2+}$ for a simulation cell containing one oxygen vacancy. Though charge-neutral cells containing defects according to Eq. 1 without adjustment of the number of electrons would be preferable, in this work, interactions between defects shall be limited. Therefore, charge-neutral cells with large distances between defects are virtually divided into oppositely charged cells. Charged cells are calculated by VASP assuming a neutralizing background charge, which is a valid approach as shown in literature.⁷⁸ A lattice constant of 5.49 Å was calculated for defect-free ceria using the Birch-Murnaghan equation of state, which is larger than the experimental lattice parameter due to the chosen set of parameters,⁷⁹⁻⁸¹ and applied for all calculations as performed in literature.^{51,52,82} For all calculations, the internal atomic positions in the cell were relaxed (changed to minimize the energy of the cell) without changing the lattice parameter.

The nudged elastic band method^{83,84} (NEB) was applied to investigate the transition states and the minimum energy pathways. One ionic configuration for the saddle point configuration ('image') was interpolated from the initial and final state of the migration process. Tests with more than one intermediate image between the initial and final configuration of the migration showed no differences in the migration energies. The same is true for tests using the climbing image nudged elastic band method⁸⁵ (CI-NEB). The internal atomic positions in the cell were relaxed without changing the lattice parameter. An exception is the calculation of the migration barrier $\Delta E_{el}^0(p,T)$ and volume ΔV at p = 0, where the cell volume was relaxed.

The phonon frequencies at constant volume were calculated using the finite difference

method discussed by Parlinski *et al.*⁸⁶ with the commercial software MedeA. All investigated structures were relaxed according to the parameters given above. Starting from these structures, cells with atomic displacements of ± 0.005 Å were created automatically. For all created cells the electronic ground state was calculated and the Hellmann-Feynman forces acting on the ions were used to build the force constant matrix. After Fourier transformation, the diagonalization of the dynamical matrix yielded the phonon frequencies at different q-points. No longitudinal/transverse optical splitting (LO/TO) was applied according to earlier studies.^{34,53} Phonon dispersions for the initial and the transition state of the migration showed minor contributions of imaginary frequencies at some q-points in the vicinity of the Gamma point that were disregarded symmetrically in initial and transition state in agreement with our earlier publication.³⁴

Kinetic Monte Carlo (KMC) simulations were performed according to an earlier work in a $16 \times 16 \times 16$ supercell with 49152 ions or vacancies and periodic boundary conditions.^{28,87} Random lattice configurations were used. Anion sublattices were equilibrated by 100 Monte Carlo Steps per particle. Simulations of the ionic conductivity were repeated at least ten times each with 100 Monte Carlo Steps per particle. The standard error on the conductivity results primarily from the use of different starting lattices. The migration energy model for an interaction radius of 5.49 Å and the applied energies from density functional theory are given in our earlier publication.²⁸

Results and discussion

Gd and Yb Doping at the Migration Edge

In this work, the attempt frequency for Gd and Yb doped ceria was calculated in the constant volume case as a function of the three possible migration edge configurations shown in Fig. 1. While for Sm doped ceria the attempt frequency increases linearly with the distance of the edge cations in the transition state, this simple relationship between geometry and attempt frequency fails for other dopants. Table 3 and Fig. 2 show that smaller dopant radii (compared to Ce⁴⁺) lead to lower attempt frequencies. The oxygen-vacancy exchange process through the Ce-Gd migration edge possesses a smaller attempt frequency than through the Ce-Ce edge. For Yb doped ceria, even a decrease in attempt frequency for increasing number of Yb dopants at the migration edge can be found. Surprisingly, for all three configurations (Ce-Gd, Ce-Yb and Yb-Yb), the migration barrier is larger than in pure ceria. Simple models considering only the potential energy landscape around the initial state predict that higher barriers lead to steep potential energies landscapes in the initial state and, therefore, to higher attempt frequencies. The decrease in attempt frequency for configurations with higher migration energies contradicts this assumption and emphasizes the importance of the transition state and the calculation of the phonon dispersion. Independent of this result, for either the Ce-RE or the RE-RE edge, both the migration energy and the attempt frequency increase with increasing dopant radius. This increase is steeper for the double-doped migration edge. We conclude, large dopants lead to an increase and small dopants to a decrease in attempt frequency with doping from one to two dopants at the migration edge.

Table 3: Electronic migration energies for different migration configurations, distances of the edge cations in the initial and the transition state and oxygen vacancy attempt frequencies $\nu_0(V,T)$ (Vineyard) at constant volume (V = const.)

migration	d_{IS}	d_{TS}	$d_{\rm TS} - d_{\rm IS}$	$\Delta E_{\rm el}^0 \left(V, T \right)$	$\nu_0(V,T)$
edge	(Å)	(Å)	(\AA)	(eV)	(s^{-1})
Ce-Ce	4.148	4.267	0.119	0.587	$1.47 \cdot 10^{12}$
Ce-Gd	4.145	4.253	0.108	0.694	$1.28 \cdot 10^{12}$
Gd-Gd	4.148	4.244	0.096	1.015	$2.31 \cdot 10^{12}$
Ce-Yb	4.125	4.256	0.131	0.694	$1.14 \cdot 10^{12}$
Yb-Yb	4.235	4.473	0.238	0.705	$0.97\cdot 10^{12}$

In the constant pressure case, the change in volume between the transition state and initial state ΔV is smaller in Gd and Yb doped ceria (Table 4) than in Sm doped ceria (Table 2). In fact, a decrease in ΔV with decreasing ionic radius is found. Smaller dopants lead to smaller volume expansions during the migration. As a result, the attempt frequency at constant pressure increases compared to the constant volume case by a factor of about



Figure 2: Oxygen vacancy attempt frequency according to phonon calculations for pure and Sm, Gd and Yb doped ceria in harmonic approximation calculated using the Vineyard method.

four/two for the Ce-Gd/Ce-Yb edge and three for the Gd-Gd and Yb-Yb edge at 900 K. Similar to Sm doped ceria, the change in the electronic migration energies is small.

Table 4: Electronic migration energies for different migration configurations, changes in volume between transition state and initial state ΔV and oxygen vacancy attempt frequencies $\nu_0(p,T)$ (Vineyard) at constant pressure (p=0) and 900 K

migration	$\Delta E_{\mathrm{el}}^{0}\left(p,T\right)$	ΔV	$\nu_{0}\left(p,T\right)$
edge	(eV)	$(Å^3)$	(s^{-1})
Ce-Ce	0.602	3.06	$7.67 \cdot 10^{12}$
Ce-Gd	0.724	2.67	$5.40 \cdot 10^{12}$
Gd-Gd	1.026	2.20	$7.55 \cdot 10^{12}$
Ce-Yb	0.732	1.59	$2.70\cdot10^{12}$
Yb-Yb	0.723	1.75	$2.48 \cdot 10^{12}$

Sm Doping in Nearest Neighborhood



Figure 3: Jump environment with a dopant in nearest neighborhood to the start position of the migrating oxygen vacancy (left). Cerium ions are green spheres, dopants are blue spheres, the oxygen ion is a red sphere and the oxygen vacancy is a red cube. On the right, the positions of the migrating oxygen vacancies are labeled start (s), center (c) and destination (d).

For Kinetic Monte Carlo simulations, the migration energies and the attempt frequencies must be known for all occurring configurations containing multiple Sm dopants and oxygen vacancies at various positions. The migration energies of all possible configurations can be calculated by combining the three explicit migration edge energies (Fig. 1) with association energies between the migrating oxygen vacancy and the other adjacent defects according to a pair interaction model proposed earlier.²⁷ In our earlier work, the attempt frequencies of the three edge configurations were assumed to be representative for all possible migration configurations.³⁴ In this study, we extend our study of the attempt frequencies to dopants near the initial position of the oxygen vacancy, which can trap the oxygen vacancy leading to an increase in migration energy. Figure 4 shows dopants in nearest neighborhood to the start position of the migrating oxygen vacancy. For the constant volume case, similar to doping at the migration edge, doping in nearest neighborhood to the start position of the migrating oxygen vacancy with one ot two Sm dopants also leads to an increase in the attempt frequency (Fig. 4 and Table 5). However, a maximum in attempt frequency is found for a single Sm dopant in nearest neighborhood to the start position.

Table 5: Electronic migration energies for different migration configurations, distances of the edge cations in the initial and the transition state and oxygen vacancy attempt frequencies $\nu_0(V,T)$ (Vineyard) at constant volume (V = const.)

cations at	d_{IS}	d_{TS}	$d_{\rm TS} - d_{\rm IS}$	$\Delta E_{\mathrm{el}}^{0}\left(V,T\right)$	$\nu_0(V,T)$
start	(Å)	(Å)	(Å)	(eV)	(s^{-1})
Ce, Ce	4.148	4.267	0.119	0.587	$1.47 \cdot 10^{12}$
Ce, Sm	4.153	4.270	0.118	0.562	$2.01\cdot10^{12}$
Sm, Sm	4.156	4.272	0.116	0.531	$1.75\cdot10^{12}$

For the constant pressure case, the attempt frequency increases monotonously with an increasing amount of Sm dopants in nearest neighborhood to the start position of the migrating oxygen vacancy (Table 6). This is surprising, as for Sm doping at the migration edge the trend for the constant volume and constant pressure case was related. For an increasing number of Sm dopants at the edge, the migration volume decreases. For an increasing number of Sm dopants in nearest neighborhood to the start position, the migration volume increases. While the volume of the supercell in the initial state is similar for dopants at the edge and the start position, the volume expansion to the transition state is stronger for dopants at the start position especially perpendicular to the direction of migration. This is surprising, as the widening of the edge cation distance increases with doping at the edge



Figure 4: Attempt frequencies for Sm doped ceria with dopants at migration edge and in nearest neighborhood to the start position of the migrating oxygen vacancy.

while it decreases with doping at the start position. The volume expansion is therefore, as shown by the relaxed structures, caused by long-range distortion.

Table 6: Electronic migration energies for different migration configurations, changes in volume between transition state and initial state ΔV and oxygen vacancy attempt frequencies $\nu_0(p,T)$ (Vineyard) at constant pressure (p=0)

cations at	$\Delta E_{\mathrm{el}}^{0}\left(p,T\right)$	ΔV	$ u_0(p,T)$
start	(eV)	$(Å^3)$	(s^{-1})
Ce, Ce	0.602	3.06	$7.67 \cdot 10^{12}$
Ce, Sm	0.593	3.26	$1.16\cdot10^{13}$
Sm, Sm	0.525	3.82	$1.37\cdot 10^{13}$

KMC Simulations with Varying Attempt Frequencies

Kinetic Monte Carlo simulations were performed with four different sets of attempt frequencies to investigate the influence of varying attempt frequencies on the ionic conductivity in Sm doped ceria. At first, fixed identical attempt frequencies for all configurations with ν_0 (V,T) from the pure ceria case were employed. Alternatively, for the three edge configurations (Fig. 1) different attempt frequencies according to the constant volume case were used (see Table 3). The last two sets of attempt frequencies consider further varying attempt frequencies: Additionally, varying attempt frequencies were introduced for dopants at the start position (Fig. 3) based on the case for a single dopant. Scaling factors, given by the quotient of attempt frequencies in doped relative to pure ceria, were multiplied to determine the change of the attempt frequencies were introduced for dopants at the start position (Fig. 2), for which the same change compared to the start position was naively assumed as a model simulation.

Figure 5 shows the very small influence on the ionic conductivity due to variations in the frequency, which are caused by doping at the migration edge positions. The reason for the small influence is the high migration energy for doped edges. Only at high dopant fractions and high temperatures, a significant influence can be found as, in this case, many doped



Figure 5: KMC simulations of the ionic conductivity of Sm doped ceria at 500 °C (left) and 1100 °C (right) with fixed and varying attempt frequencies. Experimental values according to Zhan *et al.*⁴³ and Sanghavi *et al.*⁸⁸ Lines are a guide to the eye only.

edges exist and sufficient thermal energy is available for jumps through these edges.

Varying the attempt frequency for doping of the start position has a significant influence, which starts at low temperature and intermediate dopant fractions. Vacancy jumps away from dopants in nearest neighborhood position, which free trapped vacancies and feature a large attempt frequency, appear often. Therefore, the ionic conductivity is increased.

If the same change in attempt frequency is assumed for jumps with dopants in the destination position, the ionic conductivity increases at intermediate dopants fractions and decreases at high dopant fractions for 500 °C. For 1100 °C, the ionic conductivity decreases at high dopant fractions. As an increase in attempt frequency for the destination position leads to an increase in trapping of oxygen vacancies by dopant ions, a decrease in ionic conductivity can be expected. The trapping increases at low temperature, as less thermal energy is available. Therefore, the above-described increase in conductivity is surprising. This implicates that at intermediate dopants fractions for 500 °C oxygen vacancies jump towards dopants but also easily jump away from dopants. Increasing the frequency of the trapping processes, therefore, increases the conductivity. For increasing dopant fractions, more Sm-Sm edges appear and block the migrating oxygen vacancies. In our earlier publication, we already highlighted that Sm doped ceria has one of the highest conductivities reported for a ternary cerium oxide due to its low two-step trapping properties (catch-and-hold principle).²⁸ The finding that at intermediate dopants fractions oxygen vacancies frequently jump towards and away from dopants completes the catch-and-hold principle explaining the high ionic conductivity in Sm doped ceria. At 1100 °C, considerably more thermal energy is available to cross trapping barriers so that the change in ionic conductivity is negligible. The conductivity is obviously strongly influenced by trapping, especially at low and intermediate dopant fractions, and blocking, especially at high dopant fractions. This result is in agreement with our earlier publication where we pointed out that that trapping limits the maximum value of the ionic conductivity and that blocking defines the dopant fraction of the ionic conductivity maximum.²⁸ If the presence of a dopant changes the migration energy identically for forward and backward jumps, the resulting energy contribution is referred to as *blocking*. If the change in migration energy due to doping is different for a forward and backward jump of a specific ionic configuration, the resulting energy contributions are referred to as trapping. In conclusion, the optimal dopant concentration is determined by an interplay of trapping and blocking.

A comparison between experimental ionic conductivities of the bulk domain and the result of the KMC simulations is shown in Fig. 5 (left). The experimental conductivities scatter significantly as discussed in our earlier publications.^{34,89} The trends of experimental and theoretical results are in agreement. However, the scattering in experimental values is significantly larger than changes in the simulated conductivity between the different variations in attempt frequency. Therefore, the use of varying attempt frequencies cannot be experimentally verified using conductivity measurements.

While *ab initio* calculations generally investigate microscopic properties, at the same time the macroscopic conductivity can be fitted to an Arrhenius equation (Eqs. 6 and 7) to extract the experimental apparent attempt frequency (or prefactor of diffusion) and the experimental activation enthalpy. The temperature dependence of the ionic conductivity (Fig. 5) can

be naively estimated by applying the Arrhenius equation between 500 °C and 1100 °C. For an increase in microscopic attempt frequency between the models, an increase in the experimental macroscopic attempt frequency $\overline{\nu}_{exp,V_O^{\bullet\bullet}}$ can be found. In contrast, the activation enthalpy ΔH_{a} is similar for all models. The microscopic increase in local attempt frequency does not influence the activation enthalpy. In our previous work, we showed that doping with very small amounts of Sc, which has strong trapping properties, leads to an increase in both experimental attempt frequency and activation enthalpy at low and intermediate temperatures.³⁴ A simple model with two alternating migration barriers throughout a cubic lattice showed that the activation enthalpy is strongly influenced by the higher migration energy and the attempt frequency is strongly influenced by the distribution of migration energies. We conclude, the distribution of microscopic migration energies influences both macroscopic attempt frequency and activation enthalpy. The distribution of microscopic attempt frequencies influences the macroscopic attempt frequency but has only a small influence on the activation enthalpy. Correlations between the macroscopic $\overline{\nu}_{\exp,V_O^{\bullet\bullet}}$ and ΔH_a as discussed in literature⁹⁰⁻⁹⁴ are, therefore, in the case of differently doped materials, caused by a change in the microscopic distribution of migration energies.

Conclusions

In this work, the influence of the local jump environment on the attempt frequency was investigated using density functional theory calculations. For doping at the migration edge, large dopants lead to an increase and small dopants to a decrease in the attempt frequency. In this way, doping can cause an increase in migration energy and a decrease in attempt frequency. For individual edge configurations, migration energies and attempt frequencies increase with increasing dopant radius. This increase is steeper for the double-doped migration edge. Sm doping in nearest neighborhood to the start position of the migrating oxygen vacancy also leads to an increase in attempt frequency for more dopants. Kinetic Monte Carlo simulations predict a very small influence on the ionic conductivity if varying attempt frequencies for different jump environments are considered. At intermediate dopants fractions, common diffusion paths cross dopant sites explaining why Sm doped ceria has one of the highest conductivities reported for a ternary cerium oxide due to its low two-step trapping properties. Trapping determines the conductivity at low and intermediate dopant fractions. Blocking determines the conductivity at high dopant fractions. While a distribution of microscopic migration energies influences both macroscopic attempt frequency and activation enthalpy, a distribution of microscopic attempt frequencies influences the macroscopic attempt frequency but has only a small influence on the activation enthalpy.

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Figure 6: TOC Graphic

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