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A combined DFT + *U* and Monte Carlo study on rare earth doped ceria

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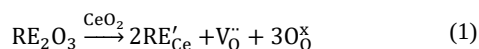
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We investigate the dopant distribution and its influence on the oxygen ion conductivity of ceria doped with rare earth oxides by combining density functional theory and Monte Carlo simulations. We calculate the association energies of dopant pairs, oxygen vacancy pairs and between dopant ions and oxygen vacancies by means of DFT+*U* including finite size corrections. The cation coordination numbers from ensuing Metropolis Monte Carlo simulations show remarkable agreement with experimental data. Combining Metropolis and Kinetic Monte Carlo simulations we find a distinct dependence of the ionic conductivity on the dopant distribution and predict long term degradation of electrolytes based on doped ceria.

I. Introduction

During the last decades, producing clean energy efficiently has become a major topic in scientific research due to the pressing issues of air pollution and global warming. One effective approach is the direct conversion of fuel and oxygen to electrical energy using solid oxide fuel cells (SOFC). The performance of these cells is significantly determined by the oxygen ion conductivity of their electrolytes. The best known material for this purpose is yttria-stabilized zirconia (YSZ) which exhibits sufficient ionic conductivities only at elevated temperatures (*ca.* 1300 K).¹ However, high operation temperatures can lead to enhanced degradation and thus lower lifespan of the fuel cells. An alternative material of interest is cerium oxide (CeO₂, ceria) doped with a rare earth oxide (RE₂O₃). Using Kröger-Vink notation the dissolution of RE₂O₃ into ceria can be described by eqn (1)



showing that positively charged oxygen vacancies V_O'' are introduced to compensate the negative charge of RE'_{Ce} cations. The high oxygen ion conductivity of doped ceria at intermediate temperatures (773–973 K) is due to the higher mobility of oxygen vacancies compared to YSZ.¹ The ionic conductivity varies depending on the type of the rare earth oxide and the doping level. Among the different rare earth oxides the highest ionic conductivity was reported by Yahiro *et al.*² for samarium (SDC) and gadolinium (GDC) doped ceria. The same authors also found a maximum in ionic conductivity at approximately 20 atom-% for SDC.³ Although a lot of experimental^{4–6} as well as theoretical research^{7–19} was conducted in recent years, the exact reason for the maximum remains incompletely explained. One explanation for the decrease in conductivity at high rare earth fractions is the

attraction of oxygen vacancies to the trivalent rare earth ions which leads to the trapping of oxygen vacancies and lowered oxygen ion mobility. Furthermore, rare earth ions with larger ionic radii can result in a higher jump barrier for oxygen ions. In each jump the oxygen ion has to cross a ‘migration edge’ formed by two neighbouring cations. The occupation of this edge with rare earth ions that are larger than the cerium ion increases the energy barrier (edge energy) for the respective jump.^{12,20–22} Another possible explanation is the repulsion and ordering of the oxygen vacancies.^{5,23}

Computational studies on the conductivity of ceria are often based on Molecular Dynamics (MD) using empirical pair potentials.^{24,25} The advantage of Monte Carlo methods that are used in this study is the possibility to activate and deactivate different interactions in the lattice and investigate their influence on the ionic conductivity.

First simulations to predict the oxygen ion conductivity of doped ceria based on a Kinetic Monte Carlo (KMC) approach were performed by Murray *et al.*⁹ using migration energies for oxygen ion jumps from empirical pair potentials. A simple model for the calculation of migration energies from density functional theory (DFT) was proposed by Nakayama and Martin¹² using a linear combination of association energies and edge energies. Based on this model Grope *et al.*²² simulated the oxygen ion conductivity of doped ceria using KMC. Further KMC simulations on doped ceria were performed by Dholabhai *et al.*^{19,26} as well as Oaks *et al.*²⁷ However, all simulations were performed using randomly distributed dopants in the cation lattice, thus neglecting the effects of dopant ordering on the oxygen ion conductivity. The assumption of a random cation distribution may be justified by the fact that the solid solution of CeO₂ and RE₂O₃ is normally prepared by mixing both oxides or by following the co-precipitation route. Then, in the as-prepared

solid solution $\text{Ce}_{1-x}\text{RE}_x\text{O}_{2-x/2}$ the cations may be distributed randomly. As it is well known that cation diffusion in the fluorite structure is very slow²⁸ the ordering of the cations at the operation temperature of the SOFC *i.e.* the time to reach the equilibrium distribution of the cations can take several years depending on operation temperature. However, SOFCs are expected to have an operation time of several years, and the ordering of cations may gain importance in the long term degradation of the ionic conductivity of oxygen ion conductors as observed experimentally.²⁹

For this reason we combined DFT+U and Monte Carlo methods to study the correlation between the defect distribution and the oxygen ion conductivity of rare earth doped ceria. We calculated association energies for defects in doped ceria from first principles for different defects and for different distances between the defects. With these energies we performed Metropolis Monte Carlo³⁰ (MMC) simulations to predict the distribution of rare earth ions and oxygen vacancies in doped ceria in thermodynamic equilibrium. The lattices obtained from the MMC simulations were used as starting configurations for Kinetic Monte Carlo simulations in order to investigate the oxygen ion conductivity for different defect distributions. We would like to point out that the aim of this study is the investigation of the influence of doping and dopant ordering on the oxygen ion conductivity rather than the prediction of absolute values of the conductivities. In this way we want to contribute to a better understanding of electrolyte degradation.

It is known that under oxygen poor conditions ceria can be reduced leading to the formation of polarons^{31,32} and a number of theoretical studies has been dedicated to this subject^{33–38}. However, we restrict our simulations to conditions where the number of polarons is much smaller than the dopant level and can thus be neglected.

The paper is organized as follows: In part II we introduce the implemented Metropolis and Kinetic Monte Carlo algorithm as well as the underlying model of pair interactions. Subsequently we describe the general DFT setup for the calculation of association energies and edge energies. In part III we present the results of our DFT calculations and the trends found for the different interactions and rare earth ions. Using these energies, we simulate the defect distribution in doped ceria and investigate its influence on the oxygen ion conductivity using KMC simulations. In part IV we give a short summary.

II. Methods

1 Metropolis Monte Carlo Simulations

In order to determine the equilibrium defect distribution in doped ceria the Metropolis Monte Carlo algorithm³⁰ was employed. The algorithm was implemented in C++. The MT19937 random number generator,³⁹ implemented in the GNU Scientific Library,⁴⁰ was used to provide the random numbers needed for the simulations.

1. Two sublattices with periodic boundary conditions forming the fluorite structure are created with a random distribution of oxygen and oxygen vacancies in the anion lattice and a random distribution of cerium and dopant ions in the cation lattice. The fraction of oxygen vacancies is fixed by the

dopant fraction according to eqn (1).

2. The positions of two different, randomly chosen ions (or oxygen vacancy) within a sublattice are permuted and the change in energy ΔE is calculated using a model of pair interactions (see below).
3. A uniform random number z in the interval $[0,1[$ is drawn, and the permutation is accepted for numbers smaller than the Boltzmann probability p :

$$p = e^{-\frac{\Delta E}{k_B T}} \quad (2)$$

Here T is the absolute temperature and k_B is the Boltzmann constant. Otherwise (for $z \geq p$) the permutation is revoked.

4. Steps 2 and 3 are repeated until the average energy of the system does not change any more and thermodynamic equilibrium is reached. Subsequently, properties like the energy and the coordination number are averaged over $5 \cdot 10^5$ further Monte Carlo steps. Test simulations with more steps showed no influence on the results.

The dependence of the extracted properties on the size of the simulation cell was investigated. To ensure convergence all simulations were performed in a simulation cell containing $12 \times 12 \times 12$ unit cells with a total number of 20736 ions and vacancies. It should be noted that in the simulations the positions of atoms were not relaxed but the ideal positions of the fluorite structure were maintained. Nevertheless, the relaxation of atomic positions is implicitly covered by the *ab initio* energies used to calculate the change in the lattice energy ΔE . The calculation of this energy in every step is a critical point in the simulation. Since it is impossible to calculate the energy of the whole lattice by DFT methods we applied a simple pair interaction model.¹² In this case the energy E_{conf} of a configuration is calculated from the interactions of the defects (eqn (3)). There are three types of interactions: interaction of oxygen vacancies in the anion sublattice (V-V), interaction of rare earth ions in the cation sublattice (RE-RE), and interaction of rare earth ions and oxygen vacancies connecting the sublattices (RE-V).

$$E_{\text{conf}} = \sum_{i=1}^4 N_{V-V}^i \cdot \Delta E_{V-V}^i + \sum_{i=1}^2 N_{RE-V}^i \cdot \Delta E_{RE-V}^i + N_{RE-RE}^1 \cdot \Delta E_{RE-RE}^1 \quad (3)$$

Here N_{A-B}^i and ΔE_{A-B}^i denote the number and association energy of defect pairs A-B in the i -th neighbour (iNN) position, respectively. The interaction range was cut off at $5.5 \text{ \AA}$ for every defect pair since the association energy decays to a negligible value at this distance (see part III). The different interactions considered in this model are shown in Fig. 1. It should be noted, that there are two distinct V-V interactions in the 3NN distance, as there are two different geometries, one with (3bNN) and one without (3aNN) a cation between the oxygen vacancies.

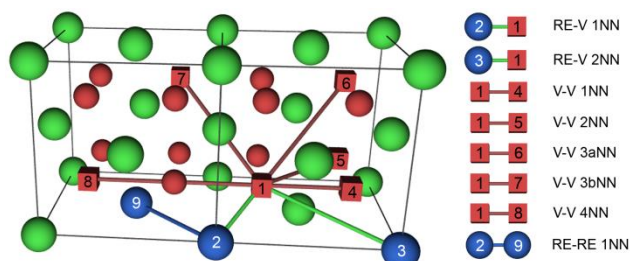


Fig. 1 2x1x1 supercell of the ceria fluorite structure with cerium ions (green), rare earth ions (blue), oxygen ions (red) and oxygen vacancies (red boxes). Interactions considered in the Metropolis Monte Carlo approach are shown. For each interaction RE-V, V-V and RE-RE the distance is denoted as i NN for the i -th nearest neighbour. There are two distinct interactions for V-V 3NN denoted as 3aNN (without a cation between the vacancies) and 3bNN (with an intermediary cation).

In experiments, properties like coordination numbers are mostly measured at room temperature. For that reason we simulate lattices at 300 K. However, it is well known that cation diffusion in ceria is orders of magnitude smaller than the oxygen diffusion.²⁸ Thus thermodynamic equilibrium for rare earth ions cannot be expected at room temperature. Therefore we apply a two-step simulation to reproduce the experimental process in a generalized form. It consists of sintering at high temperature (typically 1700 K to 2100 K in experiments) and subsequent cooling to room temperature:

1. In the first step it is assumed that at temperatures above 2/3 of the ceria melting point, *i.e.* 1500 K, rare earth ions and oxygen vacancies are mobile and all defects may adopt an equilibrium distribution. Thus, both lattices are simultaneously equilibrated at 1500 K.
2. At room temperature oxygen vacancies (or oxygen ions) are still mobile while cations are not. Thus, in the second step only the anion lattice is further equilibrated while the cation lattice is kept fixed. However, in this case interactions of rare earth ions and oxygen vacancies are still taken into account.

Metropolis Monte Carlo simulations were carried out for $\text{Ce}_{1-x}\text{RE}_x\text{O}_{2-x/2}$ within the range from $x = 0.005$ to $x = 0.5$ with a step size of 0.005. Each simulation point (shown in part III) was obtained by averaging over 20 individual simulations.

2 Kinetic Monte Carlo Simulations

The Kinetic Monte Carlo algorithm⁴¹ was implemented in C++ in a similar way like the MMC algorithm, using the MT19937 pseudo random number generator³⁹ and has already been successfully applied in a previous study.²² Simulation cells containing 16x16x16 ceria unit cells and periodic boundary conditions were used. To ensure good statistics, 10-40 cells were simulated and the results were averaged depending on the variance of the ionic conductivity.

In each step of the simulation an oxygen vacancy and a jump direction are randomly chosen. The migration energy E_{mig} of this possible jump event, which is the energy barrier between initial and final state, is calculated. The corresponding Boltzmann probability $p = \exp(-\frac{E_{\text{mig}}}{k_B T})$ is compared to a uniform random number $[0,1]$ and the jump is performed if the random number is smaller than p . The algorithm is repeated until the number of successful simulation steps reaches a pre-specified number of

Monte Carlo Steps per particle (MCS/P) where the number of particles corresponds to the number of oxygen ions.

The migration energy E_{mig} depends on the current ionic lattice configuration. Within the present computational limits it is not possible to calculate all occurring configurations by means of DFT due to their vast amount. Therefore we model the migration energy using (a) calculated edge energies and (b) pair interactions.

The migration of oxygen ions or vacancies is considered between adjacent tetrahedral oxygen sites as shown previously.¹² Along this migration pathway two cations form a ‘migration edge’. In pure CeO_2 only cerium ions are at the migration edge, while doping with rare earth oxides leads to configurations with one or two rare earth ions at the migration edge (Fig. 2). These edge energies E_{edge} are explicitly calculated using DFT (see next section).

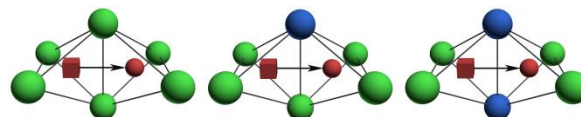


Fig. 2 Possible migration edge configurations in rare earth doped ceria. Ce-Ce edge (left), Ce-RE edge (middle) and RE-RE edge (right). Cerium ions (green), rare earth ions (blue), oxygen ions (red) and oxygen vacancies (red boxes).

Further configurations can emerge due to additional defects on neighbouring sites. These configurations are modelled by introducing pair interaction energies. The configuration energies E_{conf} for the final and the initial state of the oxygen ion jump are calculated according to eqn (3) using only the V-V and RE-V pair interactions. To calculate the resulting migration energy E_{mig} we use a linearized energy model (Fig. 3) as described in literature^{42–44} where half of the change in configurational energy ($\Delta E_{\text{conf}} = E_{\text{conf,final}} - E_{\text{conf,initial}}$) between final and initial state is added to the edge energy:

$$E_{\text{mig}} = E_{\text{edge}} + \frac{\Delta E_{\text{conf}}}{2} \quad (4)$$

Rare earth ions and oxygen vacancies are only taken into account when they are within a distance of 4.7 Å from the migrating vacancy. Larger distances will be investigated in a further study.

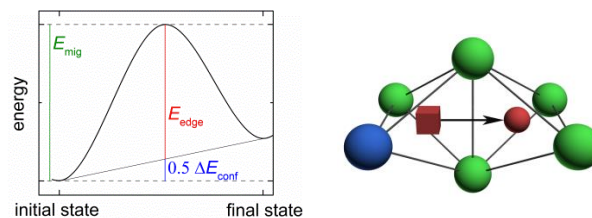


Fig. 3 Total energy depending on the reaction coordinate of an oxygen vacancy jump (left) and corresponding initial state of the migration (right).

If a small electric field²² ϵ is applied in x -direction the oxygen ion conductivity is given by $\sigma = \frac{\langle x \rangle}{\epsilon t} q n$, where $\langle x \rangle$ is the mean displacement of all oxygen ions in field direction, q the oxygen ion charge and n the concentration of oxygen ions. t is the physical time span simulated $t = \frac{N}{6N_v v_d}$, with the number of jump attempts N , the number of oxygen vacancies N_v and the attempt

frequency ν_0 which is assumed to be a constant scaling factor of 10^{13} Hz.²² A linear dependence between $\langle x \rangle$ and t was found as expected (see Fig. S1).

Because the value of ν_0 is not exactly known and the experimental data for oxygen ion conductivity in doped ceria show some scattering we do not aim to reproduce absolute values of the oxygen ion conductivity but concentrate on the influence of defect interactions and different simulation lattices. It is further noted that for each jump event only an average time is calculated in order to predict the total oxygen ion conductivity, and thus the contribution of a specific jump configuration to the conductivity remains unknown.

Pair correlation functions for different species in the simulation cell were found to be identical for simulations without and with the electric field, clearly demonstrating that the thermodynamic equilibrium is not changed by the external electric field.

In this study two techniques are combined to speed up the KMC simulations: dynamic renormalization of the Boltzmann probabilities and ‘MMC equilibrated lattices’.

In our earlier study the Boltzmann probabilities were normalized in a way that the jump with the highest probability is accepted every time.²² In this study the first $2 \cdot 10^6$ simulation steps were used to renormalize the Boltzmann probabilities to the probability corresponding to the lowest occurring energy, gaining a computational speedup of up to one order of magnitude without loss of accuracy. No jumps were observed with a renormalized probability greater than one during the main KMC run.

Starting from a random lattice, a pre-run has to be performed in KMC to reach thermal equilibrium regarding the distribution of the oxygen vacancies, which takes a large amount of computation time.²² Instead we use now the much faster MMC algorithm to equilibrate the oxygen vacancies in the lattices before starting the KMC simulation. Thus the time consuming pre-run can be disregarded, leading to a decrease in simulation time up to a factor of two orders of magnitude.

Beside the benefit of the vast computational speedup, MMC allows to simulate different cation distributions. This is of particular interest as this study aims to study the influence of dopant ordering on the oxygen ion conductivity which is generally neglected in other studies.^{9,22} The lattices are simulated as described in the MMC section; firstly simultaneous equilibration of dopants and oxygen vacancies at a given temperature T_1 , secondly equilibration of the vacancies at the KMC simulation temperature T_2 ensuring the thermodynamic equilibrium of the oxygen vacancies. In this study three types of cation lattices were used.

1. RND: a random cation lattice. This corresponds to infinite temperature T_1 and is used in most KMC simulations in literature.
2. EQ: an equilibrated cation lattice. This lattice is equilibrated at $T_1 = 1500$ K, in order to imitate the dopant distribution in the typical experimental process as described in the MMC section. This lattice corresponds to a non-aged electrolyte at the operation temperature T_2 .
3. DEG: a degraded cation lattice. This lattice is always equilibrated at the KMC temperature ($T_1 = T_2$). The lattice corresponds to an electrolyte where the dopants are ordered in

thermodynamic equilibrium of the operation temperature. As the diffusion of cations in ceria is very slow the ordering process can take years. Regarding this, the DEG lattice is a limiting case for long term degradation due to dopant ordering.

We emphasize that MMC and KMC simulations yield identical results for the oxygen vacancy distribution in equilibrium, justifying our approach to use ‘MMC equilibrated lattices’ in the KMC simulations. With 200 MCS/P the statistical error of the simulation is smaller than the statistical fluctuation due to the different input lattices. All statistical errors have been properly propagated and are displayed in part III.

3 Density Functional Theory

General computational setup

The pair association energies ΔE_{A-B}^i and edge energies were calculated by means of density functional theory within the generalized gradient approximation (GGA) according to Perdew, Burke and Ernzerhof⁴⁵ (PBE) and the projector augmented-wave method⁴⁶ (PAW) using the Vienna Ab initio Simulation Package (VASP).^{47,48} Plane waves with an energy cut-off of 500 eV and a $6 \times 6 \times 6$ Monkhorst-Pack k -point mesh for the Fm $\bar{3}m$ fluorite unit cell were applied. The convergence parameters for electronic and ionic relaxation were set to 10^{-4} eV and 0.01 eV/Å, respectively. The $2s^2 2p^4$ electrons of the oxygen atoms and the $5s^2 5p^6 6s^2 5d^1 4f^1$ electrons of the cerium 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.⁴⁹ A value of 5 eV for the 4f-orbitals of cerium was chosen according to earlier studies.^{15,16,37} 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. $(Ce_{32}O_{62})^{4+}$ for a $2 \times 2 \times 2$ supercell containing two oxygen vacancies.

Association energies

The association energy of two defects can be obtained by calculating the energy of a cell with both defects adjacent in i -th neighbour position, E_{A-B}^i , and a cell with both defects isolated from each other, $E_{A-B}^{\text{isolated}}$, and subtracting both values.

$$\Delta E_{A-B}^i = E_{A-B}^i - E_{A-B}^{\text{isolated}} \quad (5)$$

This is valid only if the defects in the isolated case have an infinite distance leading to infinite sized cells. For finite supercells a finite size correction has to be applied. For that reason the association energies were calculated for various supercells ($2 \times 2 \times 2$, $2 \times 2 \times 3$, $3 \times 3 \times 3$) thus varying the distance between defects in the ‘isolated case’. The energies were corrected for monopole interactions of the charged defects and extrapolated to $\frac{1}{r^3} \rightarrow 0$ to account for higher order interactions with r being the distance between the defects. This correction scheme is based on the approach by Makov and Payne.⁵⁰ The approach will be referred as *one cell method*.

In an alternative approach the association energy was calculated with single defects in separated cells instead of isolated defects in one cell which will be referred as *two cell method*.

$$\Delta E_{A-B}^i = E_{A-B}^i - (E_A + E_B) + E_{\text{bulk}} \quad (6)$$

Again a monopole correction and extrapolation to infinite dilution were applied. A comparison of both methods is found in part III.

Edge energies

Energy barriers for the three migration edge configurations (Fig. 2) were calculated in a 2x2x2 supercell. The nudged elastic band method⁵¹ (NEB) was used to investigate the transition states and the minimum energy pathways. One ionic configuration for the transition state (“image”) was interpolated from initial and final state of the migration process. Tests with more than one intermediate image between initial and final configuration of the migration showed no differences in the energies. The same is true for tests using the climbing image nudged elastic band method⁵² (CI-NEB). The internal atomic positions in the cell were relaxed without changing the lattice parameter.

III. Results and Discussion

1 Ab initio Results

Defect association

The lattice constant of pure ceria was determined by fitting a Birch-Murnaghan^{53,54} equation of state to the energy for different cell volumes. A value of 5.49 Å for the cubic cell was achieved consistent with earlier studies.^{55,56,36} For all subsequent calculations the lattice parameter was fixed assuming that introduction of defects affects only the local surrounding while the total cell volume is constant.

The association energies between rare earth ions and oxygen vacancies (RE-V) were calculated for a variety of rare earth ions for the nearest (1NN) and next nearest neighbour (2NN) positions according to the *one cell method*. The energies were calculated for various supercells and extrapolated to infinite dilution as described in part II.3. The statistical error of this linear fit is below 0.01 eV for all RE-V association energies, indicating the quality of our computational method. The extrapolated values vs. ionic radius (according to Shannon⁵⁷) are plotted in Fig. 4. All rare earth ions show an attractive interaction with the vacancies as it is expected from electrostatics considering the opposite relative charges of rare earth ions and oxygen vacancies. Nevertheless, there are large differences in the absolute values of the energies, showing a monotonous trend for the 1NN position from -0.75 eV for Sc³⁺ to -0.12 eV for La³⁺. These results clearly reveal that the association energy is depending not only on the Coulomb interaction but is strongly influenced by elastic effects as already found by Andersson *et al.*⁵⁸ In fact, it is well known that association of small rare earth ions and oxygen vacancies is favoured and the attraction decreases with increasing ionic radius.⁵⁹ For that reason in Fig. 4 we plot the Coulomb energy E_{Coulomb} for the RE-V interaction in 1NN and 2NN position as calculated from eqn (7).

$$E_{\text{Coulomb}} = \frac{q_1 \cdot q_2}{4\pi\epsilon_r\epsilon_0 r} \quad (7)$$

Here q is the charge of the defect with respect to the perfect lattice, r is the defect distance, ϵ_0 is the dielectric constant for vacuum and ϵ_r is the relative dielectric constant of pure ceria

which we calculated by means of DFT to be approximately 25. In Fig. 4 one can see that the curve describing the 1NN association energies intercepts the corresponding Coulomb energy approximately at the ionic radius of the Ce⁴⁺ host cation (marked as dashed line). This suggests that a RE³⁺ ion with the same radius as the host cation would show no relevant elastic contribution but the association is only due to the Coulomb attraction. For all cations larger than Ce⁴⁺ the absolute association energy is smaller than the Coulomb energy while for Sc³⁺, which is considerably smaller than Ce⁴⁺, it is larger than the Coulomb energy. The large association energy of -0.75 eV for Sc³⁺ is in agreement with the experimental finding^{60,61} of low solubility of Sc₂O₃ in ceria, since the strong association favours clustering of Sc³⁺ and oxygen vacancies and can lead to phase separation (see Fig. S2).

In contrast to the large energy differences in 1NN positions, the energy in 2NN positions is about -0.2 eV for all rare earth ions and close to the Coulomb energy of -0.25 eV, suggesting that the elastic effect has a strong influence only on the 1NN position and decays rapidly with the distance.

A crossing of the 1NN and 2NN energies is found for a radius of approximately 1.11 Å, close to the radius of Nd³⁺. In contrast to all other calculated rare earth ions La³⁺ (1.16 Å) is the only one that shows a stronger association in the 2NN than in the 1NN position. This means that for all RE³⁺ smaller than Nd³⁺ the 1NN position next to the oxygen vacancy is preferred over the 2NN position, while for larger rare earth ions the 2NN position is favoured. This observation is in accordance with the results of Nakayama and Martin¹² and is also consistent with the calculations of Andersson *et al.*⁵⁸, where the crossing was found for Pm³⁺ (1.093 Å). Furthermore, recently Dholabhai *et al.*¹⁹ reported the preference for Sm³⁺ (1.079 Å) and Gd³⁺ (1.053 Å) to be in the 1NN position next to oxygen vacancies and for Pr³⁺ (1.126 Å) to be in the 2NN position to oxygen vacancies using DFT+U calculations, which is also in agreement with our calculations.

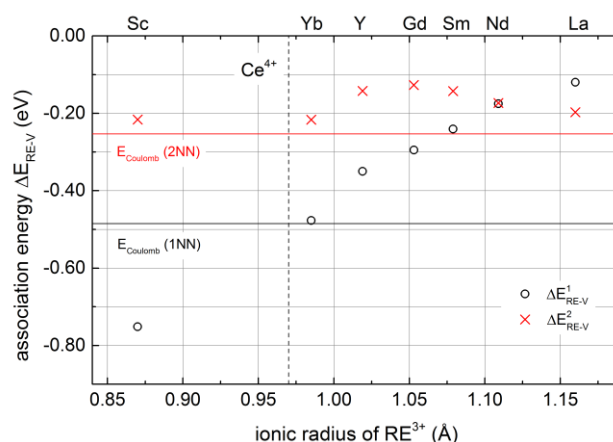


Fig. 4 Association energies of oxygen vacancies and rare earth ions in the 1NN (black circles) and 2NN (red crosses) position in ceria depending on the ionic radius of RE³⁺.⁵⁷ Negative values imply attractive interaction. The Coulomb energies for 1NN and 2NN pairs according to eqn (7) are drawn as black and red lines respectively. The radius of the Ce⁴⁺ host cation is marked as dashed line. The errors of the extrapolation to infinite dilution are within the size of the symbols.

In general, the trend of the energies shown in Fig. 4 is similar to

the one found by Nakayama and Martin¹² but with an almost constant shift of approximately 0.3 eV to more negative values. This difference can be explained by the fact that the previously calculated energies miss any kind of finite-size correction as applied in this study.

A comparison with experimental association energies is possible only for a few rare earth oxides. An early study was performed by Gerhardt-Anderson and Nowick⁵ determining the association energies of several RE-V pairs from conductivity data. The values are given in Table 1. While the general trend fits to the calculated data except for La^{3+} , our calculations show a stronger association than the experimental data. This can be explained by the fact that the calculated energies were extrapolated to infinite dilution while experimental data was gathered for small but finite concentrations. Wang *et al.*⁴ determined the association energy of the Y-V pair with impedance spectroscopy and extrapolated the values to infinite dilution. This leads to an association energy (-0.43 eV) twice as large as the value from Gerhardt-Anderson and Nowick⁵ (-0.21 eV) and even 20% larger than our calculated value (-0.35 eV). It can be seen that even the experimental association energies at low concentrations differ from the case of infinite dilution. Thus extrapolation is necessary for the experimental as well as the computational approach.

Table 1 Experimental and calculated association energies in ceria for various rare earth ions (in eV).

Rare earth ion	$\Delta H_{\text{RE-V,exp}}^5$	$\Delta H_{\text{RE-V,exp}}^4$	$\Delta E_{\text{RE-V}}^{\dagger}$
Sc^{3+}	-0.67	-	-0.75
Y^{3+}	-0.21	-0.43	-0.35
Gd^{3+}	-0.12	-	-0.29
La^{3+}	-0.14	-	-0.12

[†]This study

Calculations for the interactions of two oxygen vacancies (V-V) were performed for distances up to 6.14 Å, *i.e.* the 5th nearest neighbour position. The results in Fig. 5 show a fast decrease of the association energies after the first coordination shell whereas for the next three shells the energy is almost constant. The association energy of the fifth coordination shell is considerably small and therefore neglected in the following simulations. All energies are positive indicating repulsion of the equally charged vacancies. The 3NN vacancy interaction with a cerium ion between the vacancies (3bNN) is larger than the interaction between two vacancies without an intermediary cerium ion (3aNN).

In Fig. 5 we compare the energies calculated with the *one cell method* eqn (5) and the *two cell method* eqn (6). Although both methods were expected to yield the same extrapolated association energies there is a shift between both methods. This might be due to the fact that, because of computational limitations, only a few different supercells were used to extrapolate the association energies. However, in the case of the *one cell method* all used cells have the same charge state and we assume that the finite size errors partly cancel out. We therefore rely on the energies obtained with this method.

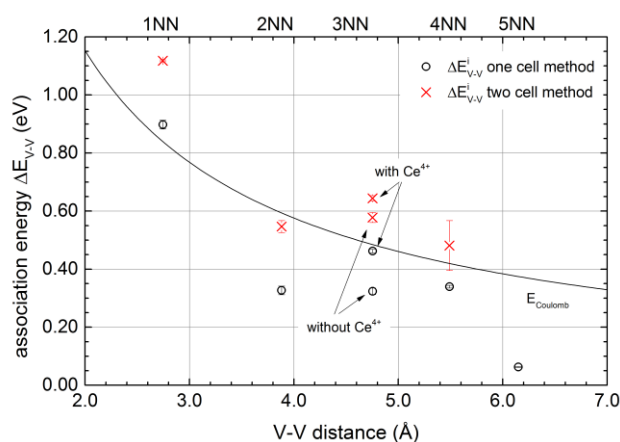


Fig. 5 Association energies of two oxygen vacancies in ceria depending on the distance for the *one cell method* (black circles) and *two cell method* (red crosses). Positive values imply repulsive interaction. The Coulomb energy according to eqn (7) is drawn as a black line. Error bars estimate the errors of the extrapolation to infinite dilution.

The nearest neighbour association of oxygen vacancies was also calculated by Nakayama and Martin¹² with a value of 0.77 eV. The difference to the value calculated in this work (0.90 eV) can be once again explained by the missing finite-size correction of the literature data, which leads to a less pronounced effect of repulsion. In Fig. 5 the Coulomb energy depending on the vacancy-vacancy distance according to eqn (7) is also plotted. The *ab initio* values are close to the Coulomb energy for all distances with some differences attributed to elastic effects.

Ismail *et al.*¹³ investigated the defect interactions in samarium doped ceria using DFT+U methods, and the trends concerning the vacancy-vacancy interaction are in agreement with our results. In their study they found a rapid decrease of the interaction energy after the first shell, an equal value for the 2NN to 4NN position and an energy minimum of nearly zero for the 5NN position.

The association energies of two rare earth ions (RE-RE) were calculated only for the first coordination shell (1NN) since the energy is already small at this distance (Fig. 6). All rare earth ions except of Sc^{3+} have similar repulsive association energies. This suggests that the interaction is mainly due to Coulomb repulsion and contains only small contributions from elastic interactions. Only Sc^{3+} shows a significantly smaller association energy which might be due to its small radius. In Fig. 6 it can be seen that the statistical error of the extrapolated association energy for some rare earth ions is relatively large, but the absolute value is below ± 0.02 eV for all energies.

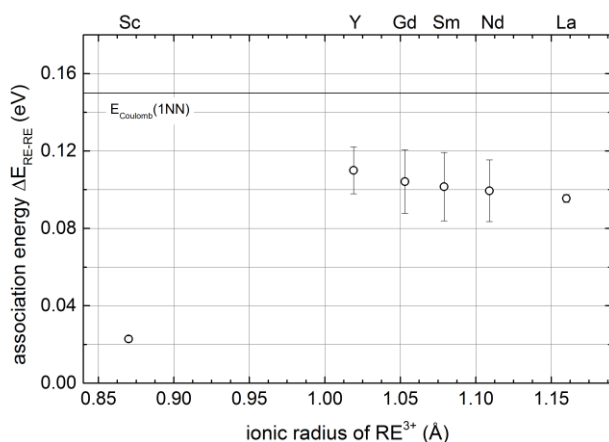


Fig. 6 Association energies of two rare earth ions in ceria for the 1NN position depending on the ionic radius of RE^{3+} .⁵⁷ Positive values imply repulsive interaction. The Coulomb energy according to eq (7) is drawn as a black line. Error bars estimate the errors of the extrapolation to infinite dilution.

Edge energies

The edge energies for the oxygen jump in pure and yttrium doped ceria (YDC) (see Fig. 2) were calculated using the DFT+U NEB method. The calculated edge energy for oxygen ion jumps in pure ceria (0.52 eV) is similar to experimental values from Steele and Floyd⁶² (0.52 eV) and Adler and Smith⁶³ (0.49 eV) (see also¹⁷). Previous theoretical calculations¹² without U potential led to slightly lower values (0.48 eV). Further theoretical values scatter between 0.46 eV^{64,65} and 0.53 eV,^{7,66} but also higher values depending on the used computational details are reported.^{67–71} Table 2 shows that the edge energy increases with increasing number of yttrium ions. Again the used U potential has only a minor effect on the calculated activation energy compared to previous calculations. Further DFT and classical calculation methods also suggest an increase in the edge energy with increasing number of yttrium ions.^{64,72,73}

Table 2 Edge energies for the three different migration edges shown in Fig. 2 (in eV).

Type of edge	Edge energy	
	this study (DFT+U)	lit ¹² (DFT)
Ce-Ce	0.52	0.48
Ce-Y	0.57	0.53
Y-Y	0.82	0.80

2 Metropolis Monte Carlo Results

Simulations applying the Metropolis Monte Carlo algorithm as described in part II were performed for ceria doped with Y^{3+} , Gd^{3+} and Sm^{3+} as these dopants reveal the best oxygen ion conductivities among the investigated rare earth oxides.⁷⁴ From the simulated lattices the coordination numbers (CN) of Ce^{4+} and RE^{3+} cations can be easily obtained by summation over all nearest neighbours. Experimental CN of doped ceria for different rare earth oxides are available from literature as follows.

The CN for a range of rare earth oxides was investigated with extended x-ray absorption fine structure (EXAFS).^{75–78} However, these literature data suffer from large scattering and seem inappropriate for the comparison with our simulations.

Coordination numbers can experimentally also be obtained by

nuclear magnetic resonance (NMR) studies but this is restricted to suitable nuclei. Among the rare earth oxides investigated in this study ^{89}Y is the only nucleus with NMR data available.

Another experimental approach to CN was developed by Nakamura⁷⁹ using the deviation of the $\text{CeO}_2\text{-RE}_2\text{O}_3$ solid solution from Vegard's law. The CN for a wide range of rare earth oxides were determined by applying a non-random distribution model to the lattice parameters obtained from x-ray diffraction (XRD) measurements. It should be noted, that the quality of the model fitting is not known and the used XRD data show some scattering.⁷⁹

In pure ceria the CN of Ce^{4+} with oxygen is eight while in doped ceria, assuming a random defect distribution, the CN for both Ce^{4+} and RE^{3+} is

$$CN_{\text{rnd}}(\text{Ce}^{4+}) = CN_{\text{rnd}}(\text{RE}^{3+}) = 8 - 2x \quad (8)$$

with x being the RE^{3+} fraction.

With an attractive interaction between oxygen vacancies and rare earth ions, $CN(\text{RE}^{3+})$ is expected to be reduced while $CN(\text{Ce}^{4+})$ should be higher than in the random distribution. This behaviour can be seen in Fig. 7 where the simulated CN of yttria doped ceria are shown along with literature values from NMR measurements. The CN obtained by NMR measurements in three different studies agree fairly well with each other suggesting a reliable measurement of the CN in contrast to EXAFS. Furthermore, the CN from NMR are in good agreement with the simulated data beside a constant, small shift of the simulation data to higher values for $CN(\text{Y}^{3+})$.

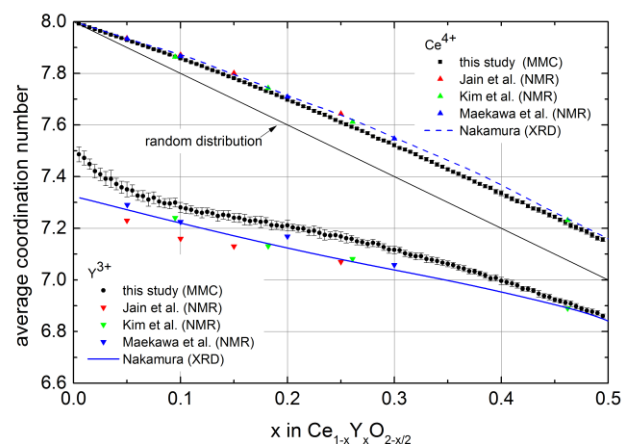


Fig. 7 Coordination numbers of Ce^{4+} and Y^{3+} in $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-x/2}$ simulated in this study (black squares and circles) and from NMR measurements (triangles) according to Jain *et al.*,⁵⁹ Kim *et al.*⁸⁰ and Maekawa *et al.*⁸¹ as well as from XRD fitting (blue lines) according to Nakamura.⁷⁹ The CN for both cations in a random distribution according to eqn (8) is drawn as black line. The CN of Ce^{4+} above and of Y^{3+} below the random distribution (line) exhibit the tendency of oxygen vacancies to be in 1NN position of Y^{3+} .

In Fig. 8 the simulated coordination numbers for the solid solution of gadolinia and ceria are shown. With the lack of other experimental data these values are compared only to CN from XRD measurements.⁷⁹ It can be seen that the simulations reproduce the experimental data quite well. The difference at high gadolinium fractions might be due to the fact that the simulations rely on a pair interaction model. For high gadolinium content the

formation of larger defect clusters can be expected and the pair interaction model might fail. In this case 'cluster interactions' between more than two defects may have to be taken into account.

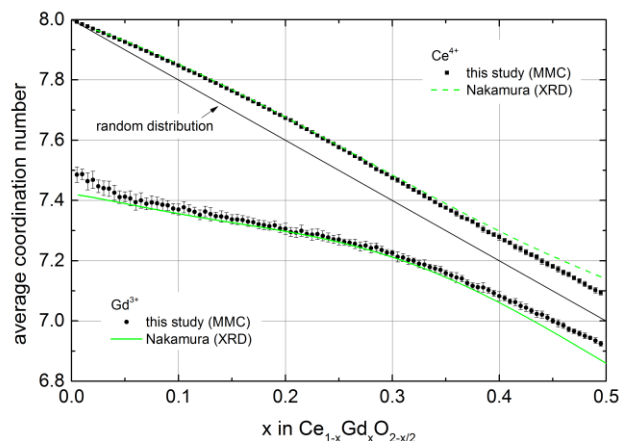


Fig. 8 Coordination numbers of Ce^{4+} and Gd^{3+} in $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-x/2}$ simulated in this study (black squares and circles) and from XRD fitting (green lines) according to Nakamura.⁷⁹ The CN for both cations in a random distribution according to eqn (8) is drawn as black line. The CN of Ce^{4+} above and of Gd^{3+} below the line exhibit the tendency of oxygen vacancies to be in 1NN position of Gd^{3+} .

The simulated coordination numbers for samarium doped ceria are shown in Fig. 9. In contrast to gadolinium and yttrium doped ceria the deviation between simulated and experimental CN from XRD is more distinct for samarium fractions above 0.3. A reason for this discrepancy might be that the CN depends sensitively on the difference between $\Delta E_{\text{RE-V}}^1$ and $\Delta E_{\text{RE-V}}^2$. For Sm^{3+} this difference is small and therefore small errors in the association energies might lead to large errors in the simulated CN. Furthermore, the deviation might be due to the fact that no 'cluster interactions' were considered.

On the other hand it should be noted that there is only one experimental reference for the CN in samarium doped ceria and it might suffer from experimental errors. Ismail *et al.*^{18,13} recently reported DFT+U calculations on samarium doped ceria. From their calculations it seems that at higher samarium concentrations the formation of Sm-V pairs in 2NN is more favoured than in 1NN position. Having this in mind, one would expect only a small deviation of the $\text{CN}(\text{Sm}^{3+})$ from the random distribution as the formation in 1NN position is less probable. In fact this is exactly what we see for the simulated data in Fig. 9. However, the results of simulation and experiment both show a higher coordination of Sm^{3+} than of Gd^{3+} i.e. a weaker trapping of oxygen vacancies by Sm^{3+} .

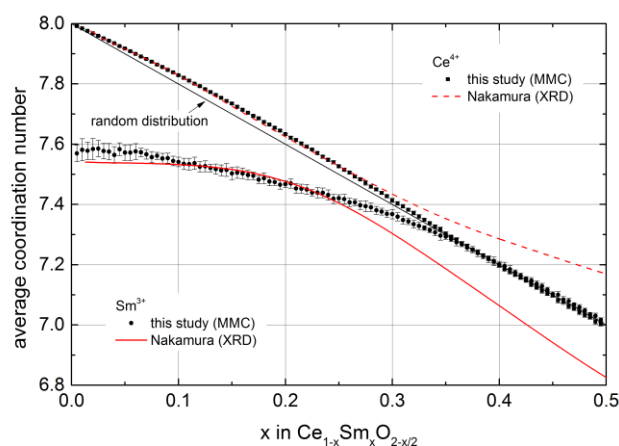


Fig. 9 Coordination numbers of Ce^{4+} and Sm^{3+} in $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-x/2}$ simulated in this study (black squares and circles) and from XRD fitting (red lines) according to Nakamura.⁷⁹ The CN for both cations in a random distribution according to eqn (8) is drawn as black line. The CN of Ce^{4+} above and of Sm^{3+} below the line exhibit the tendency of oxygen vacancies to be in 1NN position of Sm^{3+} .

We emphasize that for all investigated solid solutions the good agreement with experiment is only given when all three types of interactions (RE-V, RE-RE and V-V) are included (see Fig. S3). Exclusion of one of the interactions would lead to a significant deviation from experiment resulting in exaggerated clustering (without RE-RE or V-V interaction) or a random distribution (without RE-V interaction). On the other hand, the range of the interactions has a less pronounced effect on the coordination numbers. For example, neglecting the 4NN interaction for V-V has only a minor effect, smaller than the simulation errors.

In recent theoretical⁸² as well as experimental^{82,83} studies on yttrium doped ceria the ordering of oxygen vacancies along $\langle 111 \rangle$, i.e. in the 3NN position was found to be most favourable. Similar results were reported for yttria stabilized zirconia that crystallizes in the same structure as ceria.^{83–85} With our simulations we cannot confirm these findings. The simulated number of vacancy-vacancy pairs in different neighbouring positions is given in Fig. 10 for different fractions of yttrium in doped ceria together with the numbers in a random lattice. It can be clearly seen that in the simulated lattice the number of pairs is decreased with respect to the random distribution due to the repulsion of the vacancies, and for all yttrium fractions the 2NN pairs dominate among the investigated vacancy-vacancy pairs.

The fact that 2NN pairs are preferred can be attributed to three factors. Firstly, for each vacancy there are twelve 2NN sites but only eight 3NN sites. Secondly, while the energy of 3aNN is similar to 2NN, the repulsion of 3bNN is larger (Fig. 5). Thirdly, the 2NN pair can be stabilized by yttrium ions as there are five cation sites where yttrium ions can be in attractive interaction with both oxygen vacancies. For 3NN pairs this stabilization effect is less pronounced. In fact, simulations show that 2NN vacancy pairs with three or four yttrium ions dominate.

It should be mentioned that the ordering of vacancies might be affected by two limitations regarding the simulation model. Firstly, the accounted interactions are limited to a certain radius and more interactions might be necessary to describe a possible vacancy ordering in 3NN positions. Secondly, we used a pair interaction model that considers no cluster interactions. On the

other hand it should be mentioned that the vacancy ordering along $\langle 110 \rangle$, i.e. vacancies on 2NN positions, is in accordance with theoretical studies using classical potentials.^{86,87,23} Furthermore, in a recent DFT study Gopal *et al.*⁸⁸ reported a preference for oxygen vacancies to order along $\langle 110 \rangle$ in undoped non-stoichiometric ceria. And also experimental studies suggest a favoured ordering in $\langle 110 \rangle$ direction.⁸⁹ Thus, the ordering of oxygen vacancies in doped ceria has to be investigated further.

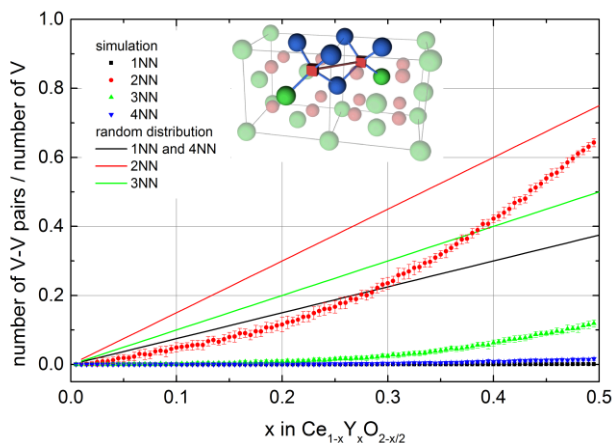


Fig. 10 Simulated number of vacancy-vacancy pairs in the first four shells (symbols) and the corresponding random distribution (lines) depending on the yttrium fraction. The 2NN pairs are favoured among the shown pairs. The inset shows a 2NN oxygen vacancy pair with possible yttrium ion positions (blue) to stabilize the vacancy pair.

3 Kinetic Monte Carlo Results

Simulations applying the Kinetic Monte Carlo algorithm as described in part II were performed for yttrium doped ceria for temperatures of 1000 K, 800 K and 700 K for lattices RND (random cation distribution), EQ (cation lattice equilibrated at 2/3 of the melting point) and DEG (fully equilibrated lattice). In Fig. 11 the oxygen ion conductivity at 1000 K is shown. The simulated conductivity curves show a maximum at typical yttrium fractions in the range of $x = 0.15$ to 0.25 as reported in literature.^{90,91} Starting at small doping fractions the conductivity first increases due to the formation of additional oxygen vacancies, but decreases when the migration energy rises due to doped migration edges (blocking, see Table 2) and trapping of oxygen vacancies at yttrium ions (see Fig 3) as shown previously.²²

The simulated conductivities of RND and EQ lattices are similar for yttrium fractions up to $x = 0.16$, whereas at higher fractions the EQ lattice shows a slightly higher conductivity. The conductivity of the fully equilibrated lattice (DEG) is considerably smaller for most yttrium fractions.

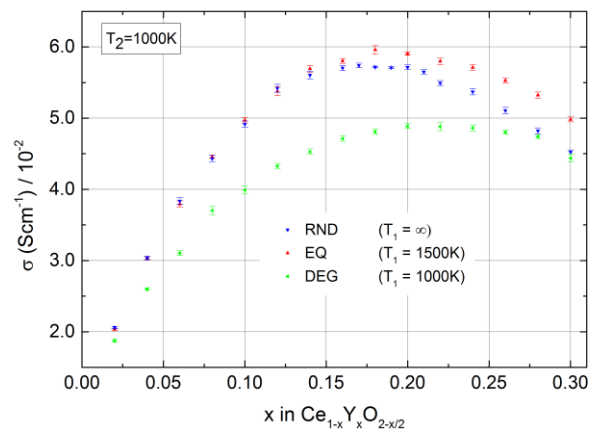


Fig. 11 Simulated oxygen ion conductivity of $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-x/2}$ at 1000 K for different lattices: random cation distribution (RND, blue), cations equilibrated at 1500 K (EQ, red) and cations equilibrated at 1000 K (DEG, green).

The origin of the difference in the oxygen ion conductivities is investigated using two properties: The number of defect pairs in the lattices obtained from MMC simulations and the number of oxygen jump attempts in different ionic configurations during a KMC run.

From the simulated lattices the number of different defect pairs in the thermodynamic equilibrium can be extracted. During a KMC run the systems stays in a steady state designed not to change this thermodynamic equilibrium. The used KMC algorithm generates jump attempts and accepts them with the corresponding Boltzmann probability $p = \exp(-\frac{E_{\text{mig}}}{k_B T})$. The number of specific jump attempts is a measure for the number of specific jump configurations of a randomly chosen and randomly jumping oxygen vacancy.

The distribution of the defects in thermodynamic equilibrium is always controlled by two quantities: the number of possible configurations (configurational entropy) and the energy of every configuration (association energy). At low temperatures the defect distribution is controlled by the formation of energetically most favoured configurations while at high temperatures further configurations are possible due to the configurational entropy.

A typical energetically favoured configuration consists of an oxygen vacancy with two yttrium ions in 1NN position. In order to understand the influence of the cation ordering on the conductivity we consider three different models for the arrangement of these three defects (Fig. 12).

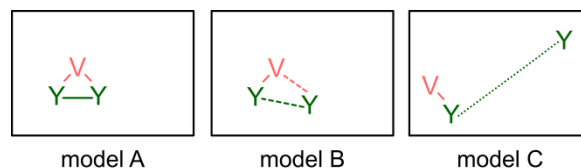


Fig. 12 Different models for the arrangement of two yttrium ions in ceria. (A) Ions in 1NN position to each other. (B) Ions in 2NN position to each other. (C) Ions separated from each other. The oxygen vacancy is always placed in an energetically favoured position.

(A) Two yttrium ions are in 1NN position as described. An approaching oxygen vacancy will be trapped due to the strong attraction to both yttrium ions in the 1NN position. Furthermore, the energy for a jump through the Y-Y edge ($E_{\text{edge}} = 0.82$ eV) is

considerably larger compared to the Ce-Ce and Ce-Y edge ($E_{\text{edge}} = 0.52$ eV and 0.57 eV respectively) making these jumps very unlikely (blocking).

(B) Two yttrium ions are in 2NN position. In this case there is no Y-Y edge and thus less blocking. Furthermore, an oxygen vacancy cannot be in the 1NN position of both yttrium ions at once, resulting in a reduced association energy which is responsible for the trapping. Even though the number of influenced anion lattice sites around the yttrium ions increases compared to model A, the Boltzmann probability of a jump increases exponentially with decreasing E_{mig} thus increasing the conductivity.

(C) Two yttrium ions are separated. The trapping is further reduced since an oxygen vacancy can only be associated to one yttrium ion.

For the RND lattice at 1000 K (Fig. 11) the yttrium ions are distributed randomly ($T_1 = \infty$) and all model configurations in Fig. 12 (A, B, C) appear based on statistics. The oxygen vacancies are distributed at lower temperature ($T_2 = 1000$ K) and prefer positions next to yttrium ions.

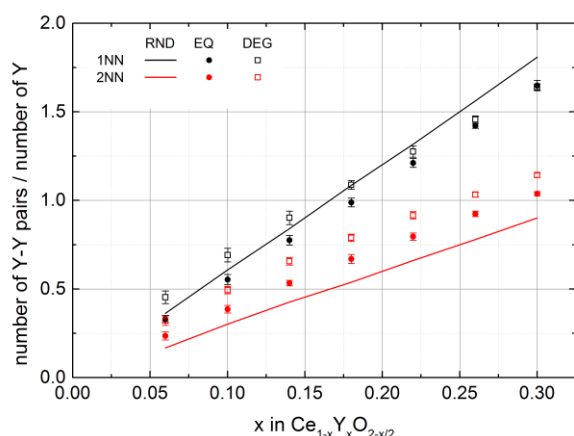


Fig. 13 Number of Y-Y pairs in 1NN (black, upper curve) and 2NN (red, lower curve) positions for lattices RND (lines), EQ (circles) and DEG (squares) at 1000 K in $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-x/2}$ as obtained from MMC simulations

In the EQ lattice the distribution of yttrium ions changes due to the lower T_1 (1500 K) as shown in Fig. 13. The number of yttrium ions in 1NN position (model A) decreases while the number of yttrium ions in 2NN position (model B) increases accordingly. This reduces the number of Y-Y edges and thus the blocking of oxygen jumps. This observation seems to be in contrast to the fact that model A is energetically more favourable than model B. A reason for this is the influence of the configurational entropy at 1500 K. Around an oxygen vacancy there are only four 1NN cation sites but twelve 2NN cation sites.

In the DEG lattice the equilibration temperature of the cations T_1 is as low as T_2 (1000 K) leading to energetically more favoured configurations. In this case slightly more Y-Y 1NN pairs (model A) exist than in the EQ lattice especially for intermediate yttrium fractions (around $x = 0.14$) as seen in Fig. 13. At high yttrium fractions the number of 1NN Y-Y pairs is similar to the EQ lattice because the high yttrium fraction always favours the 1NN Y-Y pairs. Furthermore, the number of 3NN and 4NN Y-Y pair increases (see Fig. S4). This is evidence for the formation of larger yttrium clusters in the lattice which can

effectively trap the oxygen vacancies and leads to a lowered conductivity.

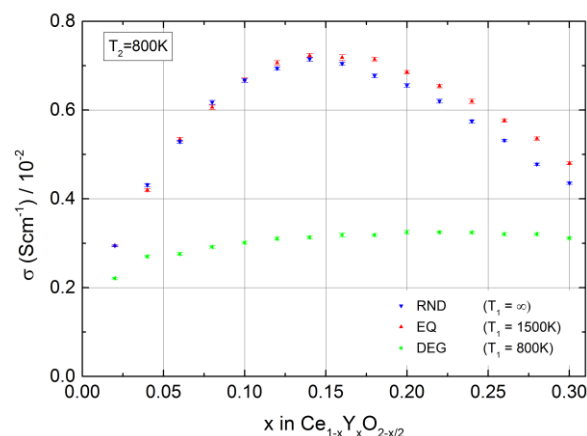


Fig. 14 Simulated oxygen ion conductivity of $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-x/2}$ at 800 K for different lattices: random cation distribution (RND, blue), cations equilibrated at 1500 K (EQ, red) and cations equilibrated at 800 K (DEG, green).

In Fig. 14 and Fig. 15 the simulated conductivities at 800 K and 700 K are shown respectively. The conductivity decreases with temperature because of the corresponding Boltzmann probability $p = \exp\left(-\frac{E_{\text{mig}}}{k_B T}\right)$. RND and EQ lattices show a similar behaviour of the conductivity at 800 K (Fig. 14) and 700 K (Fig. 15) as at 1000 K which is in agreement with the experimental values from literature.^{90,91} Since the cation distribution in RND and EQ is independent of the simulation temperature T_2 , the number of Y-Y pairs is the same for all temperatures. However, the number of jump attempts through Ce-Ce edges drops, especially at low yttrium fractions (see Fig. S5 and S6). The reason for this is the lower thermal energy which reduces the probability for oxygen vacancies to leave the association radius of yttrium ions (trapping). Furthermore, the probability of jumps through doped migration edges is reduced (blocking). As a result the maximum of the simulated conductivity is shifted to lower yttrium fractions which is in agreement with experimental data.^{90,91}

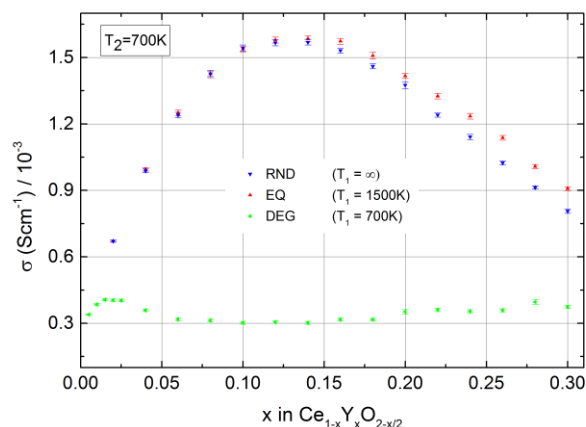


Fig. 15 Simulated oxygen ion conductivity of $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-x/2}$ at 700 K for different lattices: random cation distribution (RND, blue), cations equilibrated at 1500 K (EQ, red) and cations equilibrated at 700 K (DEG, green).

In the DEG lattices the number of specific pairs changes

compared to 1000 K as T_1 is as low as T_2 (700 K or 800 K). The described clustering of vacancies and yttrium ions increases compared to higher temperatures as can be seen from the significant increase of the Y-Y and Y-V pairs (see Fig. S7-S9). Thus, the conductivity decreases more significantly with decreasing temperature than in RND and EQ lattices.

At 800 K (Fig. 14) the conductivity is nearly constant for a broad range of yttrium fractions. The increase of the oxygen vacancies is compensated by the reduction in the mobility. The maximum of the simulated conductivity cannot be determined.

At 700 K (Fig. 15) the maximum of the conductivity is strongly shifted compared to the other lattices as a result of the ordering of the yttrium ions and the resulting increased blocking and trapping. The maximum is found at approximately $x = 0.02$. At high yttrium fractions the conductivity increases again leading to a minimum in conductivity at intermediate yttrium fractions. This behaviour could be explained by the formation of favourable pathways for the oxygen ion migration. The migration energy for every jump depends on the configuration around the oxygen vacancy in the initial and final state. Because of the strong association energy the number of 1NN Y-V pairs has the largest influence on the configurational energy. It is therefore favourable to find pathways where the number of 1NN Y-V pairs in initial and final state is equal ($\Delta N_{Y-V}^1 = 0$). For low yttrium fractions these jumps are common since in most jump configurations there is no yttrium. However, for higher fractions these jump types appear frequently only if similar migration edges are adjacent (Fig. 16 left) or occur alternating (Fig. 16 right). If this ordering takes place on larger length scales, it can be considered as a percolation path which increases the conductivity as described in literature previously.⁹²

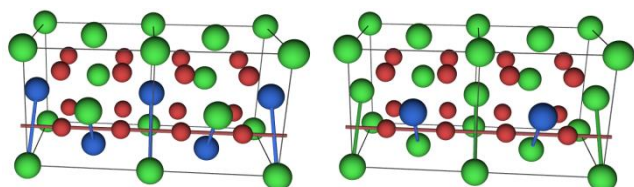


Fig. 16 Examples for two favoured migration paths in yttrium doped ceria. The favoured migration path of the oxygen is depicted as red line. On the left side there are similar adjacent migration edges while on the right side there are alternating migration edges. Cerium ions (green), yttrium ions (blue) and oxygen ions (red).

In fact, in the DEG lattice for high yttrium fractions at 700 K the number of jumps with $\Delta N_{Y-V}^1 = 0$ increases compared to the RND and EQ lattice and higher temperatures (Fig. 17). By reducing T_1 from RND lattice to EQ lattice to DEG lattice the number of jumps with $\Delta N_{Y-V}^1 = 0$ for high yttrium fractions is increased due to cation ordering.

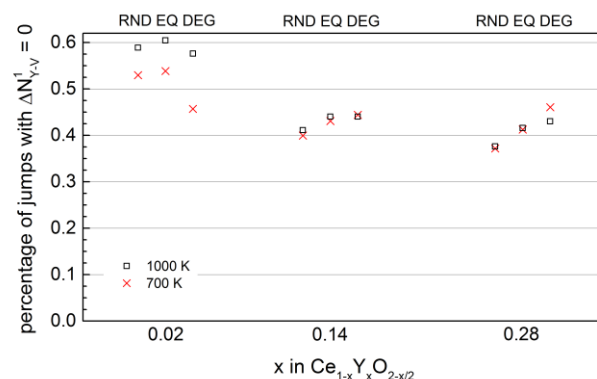


Fig. 17 Percentage of jump attempts with $\Delta N_{Y-V}^1 = 0$ at 700 K (red crosses) and 1000 K (black squares) for the three types of lattices for low, intermediate and high yttrium fractions.

As can be seen in the left part of Fig. 16 the percolation path is favoured for configurations where two yttrium ions are in 1NN position to a vacancy. Indeed, the number of such configurations is larger in the DEG lattice at 700 K than in the EQ lattice (see Fig. S10) supporting the assumption of a percolation path. If such a path exists through parts of the lattice, the migration of oxygen is enhanced and thus the conductivity rises at high yttrium fractions as seen in Fig. 15.

IV. Conclusion

We calculated the association energies of different defects at different distances in rare earth doped ceria by means of DFT+U including the correction of finite size effects. The association energies for RE-RE pairs, V-V pairs and RE-V pairs and their trend agree with computational and experimental findings from literature. Using these energies we simulated the coordination numbers of cations in doped ceria and found a remarkable agreement with experimental data for yttrium and gadolinium doped ceria. We could show that all defect interactions (RE-RE, V-V and RE-V) have to be considered to get good agreement with experiment. In our simulations of yttrium doped ceria we found a preferred ordering of oxygen vacancies along $\langle 110 \rangle$.

The oxygen ion conductivity of yttrium doped ceria was simulated using a Kinetic Monte Carlo algorithm for different yttrium distributions. We reduced the computation time by at least one order of magnitude by combining MMC and KMC simulations and found good agreement of the conductivity with experimental data. Furthermore, our results suggest that the yttrium distribution has a clear effect on the conductivity of the material. Lattices which are equilibrated at intermediate temperatures show a decreased conductivity. This degradation effect appears due to the ordering of yttrium ions and oxygen vacancies leading to increased trapping and more blocking migration edges. The ordering process requires cation diffusion which is very slow and thus it might take several years at typical operation temperatures of solid oxide fuel cells. However, the results of our simulations can be seen as limiting case for long term degradation due to cation ordering.

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Notes and references

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- ¹ B.C.H. Steele and A. Heinzel, *Nature*, 2001, **414**, 345.
- ² H. Yahiro, *Solid State Ionics*, 1989, **36**, 71.
- ³ H. Yahiro, Y. Eguchi, K. Eguchi and H. Arai, *J. Appl. Electrochem.*, 1988, **18**, 527.
- ⁴ D. Wang, D. Park, J. Griffith and A. Nowick, *Solid State Ionics*, 1981, **2**, 95.
- ⁵ R. Gerhardt-Anderson and A. Nowick, *Solid State Ionics*, 1981, **5**, 547.
- ⁶ K. Eguchi, T. Setoguchi, T. Inoue and H. Arai, *Solid State Ionics*, 1992, **52**, 165.
- ⁷ V. Butler, C. Catlow, B. Fender and J. Harding, *Solid State Ionics*, 1983, **8**, 109.
- ⁸ C. Catlow, *Solid State Ionics*, 1984, **12**, 67.
- ⁹ A. Murray, G. Murch and C. Catlow, *Solid State Ionics*, 1986, **18/19**, 196.
- ¹⁰ M. Martin, *Z. Phys. Chem.*, 2005, **219**, 105.
- ¹¹ M. Martin, *J. Electroceram.*, 2006, **17**, 765.
- ¹² M. Nakayama and M. Martin, *Phys. Chem. Chem. Phys.*, 2009, **11**, 3241.
- ¹³ A. Ismail, J.B. Giorgi and T.K. Woo, *J. Phys. Chem. C*, 2012, **116**, 704.
- ¹⁴ J. Hooper, A. Ismail, J.B. Giorgi and T.K. Woo, *Phys. Chem. Chem. Phys.*, 2010, **12**, 12969.
- ¹⁵ J. Hooper, A. Ismail, J.B. Giorgi and T.K. Woo, *Phys. Rev. B*, 2010, **81**, 224104.
- ¹⁶ P.P. Dholabhai, J.B. Adams, P. Crozier and R. Sharma, *Phys. Chem. Chem. Phys.*, 2010, **12**, 7904.
- ¹⁷ P.P. Dholabhai, J.B. Adams, P. Crozier and R. Sharma, *J. Chem. Phys.*, 2010, **132**, 94104.
- ¹⁸ A. Ismail, J. Hooper, J.B. Giorgi and T.K. Woo, *Phys. Chem. Chem. Phys.*, 2011, **13**, 6116.
- ¹⁹ P.P. Dholabhai and J.B. Adams, *J. Mater. Sci.*, 2012, **47**, 7530.
- ²⁰ F. Shimojo, T. Okabe, F. Tachibana, M. Kobayashi and H. Okazaki, *J. Phys. Soc. Jpn.*, 1992, **61**, 2848.
- ²¹ F. Shimojo and H. Okazaki, *J. Phys. Soc. Jpn.*, 1992, **61**, 4106.
- ²² B. Grope, T. Zacherle, M. Nakayama and M. Martin, *Solid State Ionics*, 2012, 476.
- ²³ D.R. Ou, F. Ye and T. Mori, *Phys. Chem. Chem. Phys.*, 2011, **13**, 9554.
- ²⁴ H. Hayashia, R. Sagawa, H. Inaba and K. Kawamurab, *Solid State Ionics*, 2000, **131**, 281.
- ²⁵ H. Inaba, R. Sagawa, H. Hayashia and K. Kawamura, *Solid State Ionics*, 1999, **122**, 95.
- ²⁶ P.P. Dholabhai, S. Anwar, J.B. Adams, P. Crozier and R. Sharma, *J. Solid State Chem.*, 2011, **184**, 811.
- ²⁷ A. Oaks, D. Yun, B. Ye, W.-Y. Chen and J.F. Stubbins, *J. Nucl. Mater.*, 2011, **414**, 145.
- ²⁸ K. Ando and Y. Oishi, *J. Nucl. Sci. Technol.*, 1983, **20**, 973.
- ²⁹ T. Zhang, J. Ma, L. Kong, S. Chan and J. Kilner, *Solid State Ionics*, 2004, **170**, 209.
- ³⁰ N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller and E. Teller, *J. Chem. Phys.*, 1953, **21**, 1087.
- ³¹ H. Tuller and A. Nowick, *J. Phys. Chem. Solids*, 1977, **38**, 859.
- ³² R. Farra, M. García-Melchor, M. Eichelbaum, M. Hashagen, W. Frandsen, J. Allan, F. Girsdsies, L. Szentmiklósi, N. López and D. Teschner, *ACS Catal.*, 2013, **3**, 2256.
- ³³ M. Ganduglia-Pirovano, J. Da Silva and J. Sauer, *Phys. Rev. Lett.*, 2009, **102**, 26101.
- ³⁴ M. Nakayama, H. Ohshima, M. Nogami and M. Martin, *Phys. Chem. Chem. Phys.*, 2012, **14**, 6079.
- ³⁵ P.R.L. Keating, D.O. Scanlon, B.J. Morgan, N.M. Galea and G.W. Watson, *J. Phys. Chem. C*, 2012, **116**, 2443.
- ³⁶ T. Zacherle, A. Schrieffer, R. de Souza and M. Martin, *Phys. Rev. B*, 2013, **87**, 134104.
- ³⁷ S. Grieshammer, T. Zacherle and M. Martin, *Phys. Chem. Chem. Phys.*, 2013, **15**, 15935.
- ³⁸ J.J. Plata, A.M. Márquez and J.F. Sanz, *J. Phys. Chem. C*, 2013, **117**, 25497.
- ³⁹ S. Konuma, *IEICE Transactions on Information and Systems*, 2005, **88**, 2876.
- ⁴⁰ M. Galassi, J. Davies, J. Theiler, B. Gough, G. Jungman, M. Booth and F. Rossi, in *GNU Scientific Library: Reference manual*, Network Theory, Bristol, 2009.
- ⁴¹ G.E. Murch, *Am. J. Phys.*, 1979, **47**, 78.
- ⁴² A. Van der Ven and G. Ceder, *Phys. Rev. Lett.*, 2005, **94**, 45901.
- ⁴³ A. Van der Ven, G. Ceder, M. Asta and P. Tepesch, *Phys. Rev. B*, 2001, **64**, 184307.
- ⁴⁴ E. Lee, F. Prinz and W. Cai, *Phys. Rev. B*, 2011, **83**, 52301.
- ⁴⁵ J.P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.
- ⁴⁶ P. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953.
- ⁴⁷ G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.
- ⁴⁸ G. Kresse, *Phys. Rev. B*, 1999, **59**, 1758.
- ⁴⁹ S.L. Dudarev, S.Y. Savrasov, C.J. Humphreys and A.P. Sutton, *Phys. Rev. B*, 1998, **57**, 1505.
- ⁵⁰ G. Makov and M. Payne, *Phys. Rev. B*, 1995, **51**, 4014.
- ⁵¹ H. Jonsson, G. Mills and K. M. Jacobsen, in *Classical and quantum dynamics in condensed phased simulations*, ed B.J. Berne, G. Ciccotti and D.F. Coker, World Scientific, Singapore, River Edge, NJ, 1998.
- ⁵² G. Henkelman, B.P. Uberuaga and H. Jónsson, *J. Chem. Phys.*, 2000, **113**, 9901.
- ⁵³ F. Murnaghan, *Am. J. Math.*, 1937, **59**, 235.
- ⁵⁴ F. Birch, *Phys. Rev.*, 1947, **71**, 809.
- ⁵⁵ J. Da Silva, M. Ganduglia-Pirovano, J. Sauer, V. Bayer and G. Kresse, *Phys. Rev. B*, 2007, **75**, 45121.
- ⁵⁶ P.R.L. Keating, D.O. Scanlon, B.J. Morgan, N.M. Galea and G.W. Watson, *J. Phys. Chem. C*, 2012, **116**, 2443.
- ⁵⁷ R.D. Shannon, *Acta Cryst A*, 1976, **32**, 751.
- ⁵⁸ D. Andersson, S. Simak, N. Skorodumova, I. Abrikosov and B. Johansson, *Proc. Natl. Acad. Sci.*, 2006, **103**, 3518.
- ⁵⁹ P. Jain, H.J. Avila-Paredes, C. Gapuz, S. Sen and S. Kim, *J. Phys. Chem. C*, 2009, **113**, 6553.
- ⁶⁰ S. Yamazaki, *Solid State Ionics*, 2000, **136-137**, 913.
- ⁶¹ V. Grover, A. Banerji, P. Sengupta and A. Tyagi, *J. Solid State Chem.*, 2008, **181**, 1930.
- ⁶² B. Steele and J. Floyd, *Proc. Br. Ceram. Soc.*, 1971, **19**, 524.
- ⁶³ S.B. Adler and J.W. Smith, *Faraday Trans.*, 1993, **89**, 3123.
- ⁶⁴ D. Andersson, *Proceedings of the National Academy of Sciences*, 2006, **103**, 3518.
- ⁶⁵ J. Conesa, *Surf. Sci.*, 1995, **339**, 337.
- ⁶⁶ M. Nolan, J. Fearon and G. Watson, *Solid State Ionics*, 2006, **177**, 3069.
- ⁶⁷ N. Bulgakov, V. Sadykov, V. Lunin and E. Kemnitz, *React. Kinet. Catal. Lett.*, 2002, **76**, 103.
- ⁶⁸ G. Balducci, J. Kašpar, P. Fornasiero, M. Graziani, M.S. Islam and J.D. Gale, *J. Phys. Chem. B*, 1997, **101**, 1750.
- ⁶⁹ G. Balducci, M.S. Islam, J. Kašpar, P. Fornasiero and M. Graziani, *Chem. Mater.*, 2000, **12**, 677.
- ⁷⁰ P. Geerlings, F. de Proft, C. van Alsenoy, C. Frayret, A. Villesuzanne, M. Pouchard and S. Matar, *Int. J. Quantum Chem.*, 2005, **101**, 826.
- ⁷¹ A. Pryde, S. Vyas, R. Grimes, J. Gardner and R. Wang, *Phys. Rev. B*, 1995, **52**, 13214.
- ⁷² C. Frayret, A. Villesuzanne, M. Pouchard, F. Mauvy, J.-M. Bassat and J.-C. Grenier, *J. Phys. Chem. C*, 2010, **114**, 19062.
- ⁷³ A. Murray, G. Murch and C. Catlow, *Solid State Ionics*, 1986, **18-19**, 196.
- ⁷⁴ M. Mogensen, *Solid State Ionics*, 2000, **129**, 63.
- ⁷⁵ S. Yamazaki, T. Matsui, T. Ohashi and Y. Arita, *Solid State Ionics*, 2000, **136/137**, 913.
- ⁷⁶ H. Yoshida, H. Deguchi, K. Miura and M. Horiuchi, *Solid State Ionics*, 2001, **140**, 191.
- ⁷⁷ H. Deguchi, H. Yoshida, T. Inagaki and M. Horiuchi, *Solid State Ionics*, 2005, **176**, 1817.
- ⁷⁸ Y. Wang, H. Kageyama, T. Mori, H. Yoshikawa and J. Drennan, *Solid State Ionics*, 2006, **177**, 1681.

-
- ⁷⁹ A. Nakamura, *Solid State Ionics*, 2010, **181**, 1543.
- ⁸⁰ N. Kim and J.F. Stebbins, *Chem. Mater.*, 2007, **19**, 5742.
- ⁸¹ H. Maekawa, K. Kawata, Y.P. Xiong, N. Sakai and H. Yokokawa, *Solid State Ionics*, 2009, **180**, 314.
- ⁸² M. Burbano, S.T. Norberg, S. Hull, S.G. Eriksson, D. Marrocchelli, P.A. Madden and G.W. Watson, *Chem. Mater.*, 2012, **24**, 222.
- ⁸³ S. Hull, S. Norberg, I. Ahmed, S. Eriksson, D. Marrocchelli and P. Madden, *J. Solid State Chem.*, 2009, **182**, 2815.
- ⁸⁴ S.T. Norberg, S. Hull, I. Ahmed, S.G. Eriksson, D. Marrocchelli, P.A. Madden, P. Li and J.T.S. Irvine, *Chem. Mater.*, 2011, **23**, 1356.
- ⁸⁵ D. Marrocchelli, P.A. Madden, S.T. Norberg and S. Hull, *Chem. Mater.*, 2011, **23**, 1365.
- ⁸⁶ F. Ye, T. Mori, D. Ou, A. Cormack, R. Lewis and J. Drennan, *Solid State Ionics*, 2008, **179**, 1962.
- ⁸⁷ F. Ye, T. Mori, D.R. Ou and A.N. Cormack, *Solid State Ionics*, 2009, **180**, 1127.
- ⁸⁸ C.B. Gopal and A. van de Walle, *Phys. Rev. B*, 2012, **86**, 134117.
- ⁸⁹ D. Ou, T. Mori, F. Ye, J. Zou, G. Auchterlonie and J. Drennan, *Phys. Rev. B*, 2008, **77**, 24108.
- ⁹⁰ G. Balazs, *Solid State Ionics*, 1995, **76**, 155.
- ⁹¹ T.A. Ramanarayanan, W.L. Worrell and H.L. Tuller, in *Proceedings of the Second International Symposium on Ionic and Mixed Conducting Ceramics*, Pennington, NJ, 1994.
- ⁹² M. Meyer, N. Nicoloso and V. Jaenisch, *Phys. Rev. B*, 1997, **56**, 5961.