The role of dopant segregation on the oxygen vacancy distribution and oxygen diffusion in CeO$_2$ grain boundaries

Adam R Symington$^{1,3}$, Marco Molinari$^3$, Joel Statham$^1$, Ji Wu$^1$ and Stephen C Parker$^{1,3}$

$^1$Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, United Kingdom
$^2$Department of Chemistry, University of Huddersfield, Queensgate, Huddersfield HD1 3DH, United Kingdom
$^3$Author to whom any correspondence should be addressed.

E-mail: A.R.Symington@bath.ac.uk and S.C.Parker@bath.ac.uk

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Abstract

An important challenge when attempting to identify the role of microstructure on the properties of doped energy materials is to distinguish the behaviour of each grain boundary. In this paper we describe our recent work using atomistic simulations to investigate the structure, composition and oxygen transport of gadolinium doped cerium dioxide tilt grain boundaries. We find that energy minimisation can be systematically employed to screen grain boundary structures and dopant segregation. When dopants are distributed equally across grains, molecular dynamics simulations reveal oxygen vacancies reside near dopants, resulting in higher oxygen diffusivity. Once the dopants accumulate at the grain boundaries these grain boundaries become saturated with oxygen vacancies. We see fast oxygen diffusion within the grain boundary plane, although the depletion layer, as shown via the electrostatic potential appears to block transport across the grain boundary. However, this is highly dependent on the grain boundary structure as we find striking differences of the electrostatic potential and the segregation behaviour between each of interface studied.

1. Introduction

Fluorite structured ceramic materials, including ceria (CeO$_2$) and doped zirconia (ZrO$_2$), have attracted considerable attention for energy applications in the last three decades due to their high ionic conductivity [1, 2]. These ionic conductors find use as solid electrolytes in solid state electrochemical devices such as solid oxide fuel cells (SOFC) [3–5]. However the widespread use of such devices is hindered by material issues relating to high operating temperatures [6]. Lanthanide doped ceria materials, i.e. Ln$^{3+}$ ions like gadolinium, exhibit excellent oxygen conductivity due to the introduction of excess ionic carriers (oxygen vacancies). These doped materials, particularly gadolinium doped ceria (GDC), allow for slower material degradation as the diffusion of oxygen occurs at lower operating temperatures (600 °C–800 °C) [6–8], with further improvement obtained through a reduction of particle size [9, 10]. Thus demonstrating that the microstructure plays a key role in the material properties.

Polycrystalline GDC, similar to other doped oxides, shows defect segregation to the grain boundaries (GBs), which has been observed experimentally and is detrimental to material properties [11, 12]. As defects, particularly dopants, segregate and accumulate at the GBs, they may contribute to an increase in GB resistance to the transport of oxygen. This results in a reduction in the conductivity of polycrystals compared to single crystals [12–15]. It is therefore critically important to understand and ultimately control the processes that occur at these interfaces and how they affect the materials properties.

The degradation associated with dopant segregation at GBs in GDC has been studied theoretically to elucidate the atomistic details relating to the mechanism [16]. A hybrid Monte Carlo–molecular dynamics (MD)

* The data supporting the findings of this study are openly available at https://doi.org/10.5281/zenodo.3366185.
revealed that Gd$^{3+}$ segregation to the GBs is a thermodynamically favourable process [17], and driven by a high oxygen vacancy concentration at the GBs. However, this study was only limited to the $\Sigma 5 (310)/[001]$ tilt GB in GDC. Dholabhai et al combined MD and density functional theory to study three symmetric GDC GBs, namely the $\Sigma 3 (111)/[110]$ tilt GB, $\Sigma 5 (310)/[001]$ tilt GB and $\Sigma 5 (001) \theta = 36.87^\circ$ twist GB [18], finding that GBs have different segregation behaviour, and that the stability of dopant-vacancy clusters at GBs was heavily dependent on the local structure and dopant arrangements at the GBs.

This work builds on our previous work on dopants in UO$_2$ [19] but has been expanded to consider the effects of dopant distribution, dopant concentration and given the importance of space charge effects in CeO$_2$ [9, 14, 20, 21], the change in electrostatic potential at GBs. We present a survey of different coincidence site lattice (CSL) GBs in stoichiometric ceria and GDC with gadolinium concentration between 10% and 30%. We have considered multiple dopant distribution schemes, specifically, a uniform distribution symptomatic of freshly made devices, and a configuration with full Gd$^{3+}$ segregation at the GB symptomatic of degraded devices. The stability, dopant and oxygen vacancy segregations, electrostatic potential along with the oxygen diffusivity of these GBs are evaluated as a function of temperature and dopant concentration.

2. Methodology

Six low index tilt grain boundaries of CeO$_2$ were constructed using the METADISE code [22] with a classical potential model based on rigid ions and partial charges according to

$$U(r) = D_{ij} [(1 - e^{-a_{ij}(r-r_0)})^2 - 1] + \frac{C_{ij}}{r^{12}},$$  \hspace{1cm} (2.1)

where $D_{ij}$ is the depth of the potential energy well, $a_{ij}$ is the a function of the slope of the potential energy well, $r$ is the distance of separation, $r_0$ is the equilibrium distance between species $i$ and $j$, and $C_{ij}$ relates to the potential energy well and describes the repulsion at very short distances between species $i$ and $j$. The parameters used for each species, reported in Sayle et al, are shown in table 1 [23].

This model has been shown to accurately reproduce the structural and elastic properties of CeO$_2$ and UO$_2$ [24, 25]. GB structures were generated initially by taking each possible surface termination comprised of surface unit cells with no dipole perpendicular to the surface and scanning one surface relative to the other [26]. At each grid point in this scan a full surface relaxation is performed and as an extension to earlier approaches the lowest energy well and describes the repulsion at very short distances between species

$$\gamma_{GB} = (E_{GB} - E_{Bulk}) / A,$$  \hspace{1cm} (2.2)

where $E_{GB}$ and $E_{Bulk}$ are the energies of the GB and bulk simulations cells respectively and $A$ is the area of the GB plane.

Defect incorporation energies were investigated for the six GBs using the CHAOS code [27], namely Gd$^{3+}$ substitution at Ce$^{4+}$ sites and oxygen vacancies ($V_o$). This approach employs the Mott–Littleton method to evaluate point defect energy at every site in the simulation cell. It has the advantage of including both the electrostatic and steric contributions by including a full relaxation. Defects were incorporated at every site into each boundary, which corresponds to the GB plane and extended to a depth of approximately 30 Å perpendicular to the boundary, in order to map the energetics of the defect as a function of their distance from the GB. Defects were considered to be point defects. The energies are presented with reference to the bulk defect energy which is set to 0 eV.

All MD simulations were performed using the DL_POLY code [28]. Simulations of 4 ns employed 3 dimensional periodic boundary conditions, a timestep of 1 fs, an 8.5 Å cut-off, within a temperature range of 900–3000 K, at intervals of 300 K. Equilibration was performed for 1 ns using the NPT ensemble until unit cell volume was converged. Production simulations were carried out for 3 ns using the NVT ensemble with a Nose–Hoover thermostat. All GB structures were annealed at high temperature and then cooled down to low

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**Table 1. Potential model parameters.**

| Species | $D_{ij}$ (eV) | $a_{ij}$ ($\AA^{-2}$) | $r_0$ (Å) | $C_{ij}$ (eV Å$^{12}$) |
|---------|---------------|------------------------|------------|------------------------|
| Ce$^{4+}$O$^{-1.2}$ | 0.098 352 | 1.848 592 | 2.930 147 | 1 |
| Gd$^{3+}$O$^{-1.2}$ | 0.028 451 | 2.057 296 | 3.074 956 | 3 |
| O$^{-1.2}$O$^{-1.2}$ | 0.041 730 | 1.886 824 | 3.189 367 | 22 |
temperature using the NPT MD ensemble. The annealing allowed for the most stable structure across the wide
temperature range of each GB to form.

Figure 1 shows a schematic representation of the simulation cells and table S2 presents the size of the
simulation cells for MD simulations, typically 7500 atoms. The GB is sandwiched between grain interiors (GIs)
forming a layered structure and GBs are far apart to avoid interaction. The GB widths, represent the GB region
either side of the GB core. The GB width is the region of the structure that contains the GB and extends until the
diffusivity returns to the bulk value.

We generated configurations with fully segregated Gd\(^{3+}\) (representing a degraded SOFC device) and
configurations with Gd\(^{3+}\) distributed randomly (representing a freshly prepared device) for investigation with
MD. Stoichiometric structures were also simulated as a control, referred to as CO. Three concentrations of
Gd\(^{3+}\), 10\%, 16\% and 30\% were substituted for Ce\(^{4+}\) cations. These percentages represent the concentration of
dopants considering all Ce\(^{4+}\) cations in the simulation cell. Different doping schemes were studied;
N_GB—Gd\(^{3+}\) doped CeO\(_2\) nanolayered structures with N% random substitution of Gd\(^{3+}\) localized within the
GB regions; e.g. 10_GB represents a configuration with 10% Gd\(^{3+}\) randomly distributed within the GB regions.
N_Rand—Gd\(^{3+}\) doped CeO\(_2\) nanolayered structures with N% substitution of Gd\(^{3+}\) randomly distributed
through the entire structure, i.e. GI and GB region; e.g. 10_Rand represents a configuration with 10% Gd\(^{3+}\)
randomly distributed within the entire structure. We note that 30_GB cannot be formed within our model as
there are not enough Ce\(^{4+}\) cations within the GB regions to accommodate 30\% Gd\(^{3+}\) substitution. Oxygen
vacancies were introduced randomly to maintain charge neutrality throughout the entire structure, however
their distribution is not a concern as their mobility is such that they reached their equilibrium distribution
within the NPT MD simulation. This was confirmed by examining the evolution of the oxygen stoichiometry
over time. Oxygen vacancies segregated during the early stages of the NPT simulation and this distribution
persisted for the duration of the simulation. Diffusion data for O within a specified region was obtained from a
regional mean squared displacement (MSD) within the region of interest according to

\[
\langle r_i^2(t) \rangle = 6 D_O t, \tag{2.3}
\]

where \(\langle r_i^2(t) \rangle\) is the MSD, \(D_O\) is the diffusion coefficient for oxygen, and \(t\) is time. The calculation of the MSD
only takes into account those segments of atom trajectories for oxygen species that pass within the region of
interest e.g. the GB.

We use the residence time \(\tau\) to evaluate the average time that an oxygen atom spends in contact with each
cation (Ce\(^{4+}\) and Gd\(^{3+}\)) [29]. The \(\tau\) was calculated from the residence time correlations function, which is
defined as

\[
\langle R(t) \rangle = \left\langle \frac{1}{N_0} \sum_{i=1}^{N} \theta_i(0) \theta_i(t) \right\rangle, \tag{2.4}
\]

where \(N\) is the number of oxygen atoms within a 3 Å radius of the cation and \(\theta_i(t)\) is the heavyside function,
which is 1 if the \(i\)th oxygen atom is in the 3 Å radius at \(t\) and 0 otherwise. An oxygen atom was only considered to
have left the 3 Å radius if it did so for at least 2 ps, which allowed molecules that temporarily left then re-entered
to be included in \(\tau\). Equation (2.4) is integrated to calculate \(\tau\).
The electrostatic potential in one dimension across the GB was calculated according to
\[
\tau_r = \int_0^\infty R(t) \, dt. \tag{2.5}
\]

The electrostatic potential in one dimension across the GB was calculated according to
\[
\Delta_v(x) = -\int_{x_0}^x E(x) \, dx, \tag{2.6}
\]
where \( E(x) \) is the electric field and given by
\[
E(x) = \frac{1}{-\varepsilon_0} \int_0^x \rho_q(x) \, dx, \tag{2.7}
\]
where \( \rho_q \) is the total charge density perpendicular to the interface and \( \varepsilon_0 \) is the permittivity of free space [30].

3. Results

3.1. Stoichiometric GB structures and potential energy surfaces

The GB structures used in this study and their scans are presented in figure 2. These were chosen from a database of different tilt GB scans generated during this study (figure 3). These six tilt GBs are low Miller index surfaces with low formation energies. The \( \Sigma3(111) \), \( \Sigma5(210) \), \( \Sigma5(310) \), \( \Sigma9(221) \), \( \Sigma11(311) \) and \( \Sigma19(331) \) boundaries have all been observed experimentally, suggesting they are low energy and are present in significant concentrations within polycrystalline fluorite samples [31–34]. The scans relate to the symmetry of the surfaces and enables us to infer the energy barriers to processes such as GB sliding and also the depth of the energy well, which reflects the likelihood of the boundary forming.

3.2. Dopant segregation energy at GB

Once the most stable structure of a specific GB is found, point defect segregation energies were calculated. Figure 4 shows the defect segregation energy profiles for the \( \Sigma19(331) \) GB as example, with the rest being included in the SI (figure S1 is available online at stacks.iop.org/JENERGY/1/042005/mmedia). In all cases, the GB regions (defined from \(-15 \) to \(15 \) Å with the GB core at \(0 \) Å) were found to be energetically favourable to accommodate both Gd\(^{3+}\) and oxygen vacancies \( (V_o) \) \((0.15–0.2 \text{ eV per defect})\), which is in agreement with previous computational work on specific GB structures [17, 18]. Although most sites are energetically favourable for a defect to segregate, some specific sites within the GB region were calculated to have slightly higher energies with respect to energies of defects located in the bulk regions outside of the GB. This behaviour implies that
segregation of dopants is site dependent within a specific structure and will be missed if considering only average properties of each plane of atoms.

We have also used MD simulations to evaluate the impact of temperature and dopant concentration on the energetics of Gd segregation. In this case by comparing the N_GB models where all the dopants are in the GBs, to the N_Rand models where Gd$^{3+}$ dopants are randomly distributed throughout the entire structure. The difference in configurational energy between the two N_GB and N_Rand configurations (10% and 16% concentrations) is shown in figure 5. The data indicates that the energetic contribution favours Gd$^{3+}$ segregation at the GBs rather than random distribution in all models evaluated. This is in line with experimental evidence [32, 35] and is supported by our defect segregation energies, which neglect temperature (figures 4 and S1). Increasing temperature increases segregation energies until about 2700 K, beyond which the GBs start to melt.

3.3. Doped GB structure

On random introduction of Gd$^{3+}$ ions over the entire simulation cell (N_Rand) the stoichiometric GB structures are retained. However, when Gd$^{3+}$ was segregated within the GB regions (N_GB), there are significant structural rearrangements during the annealing (figure 6). The Σ3(111) GB undergoes a shift parallel to the GB plane with the cation arrays converging into the middle of the GB pipes. The presence of impurities promotes an alteration to the structure of the Σ5(210) with similar structural changes previously reported for stoichiometric UO$_2$ [25], but not yet for GDC. However previous studies on Gd$^{3+}$ segregation in GDC GBs are based on a static model of un-doped CeO$_2$ [17, 18], where the composition of GDC is considered to be a dilute solution of point
defects and temperature is neglected. We recognise that the concentration of Gd in the N_GB models is relatively high, thus may not be representative of many experimental studies. However our results are the first that show that high concentrations of Gd can cause an alteration in GB structure, which may impact those experimental sample of doped nanoceria with high concentration of Gd [10].

A possible explanation for these structural rearrangements is that the dopants stabilise metastable GB configurations at higher temperatures, which may be energetically inaccessible under stoichiometric conditions, although these structures may be present in the potential energy surfaces presented in figure 3. It is worth noting that the GDC material is used at relatively high temperatures (600–1000 K or higher) [36] in thermochemical devices, thus the GB structures are likely to change over time. Therefore, the segregation triggered structural transformations is likely to be important in the study of the long-term degradation behaviour of GDC.

3.4. Oxygen vacancy segregation at GBs

We have quantified the distribution of oxygen vacancies ($V_o$) within the doped configurations as the $V_o$ concentration within the two regions per Å$^3$ i.e. the GI and the GB regions (figure 7). In the N_GB, there is almost complete depletion of $V_o$ in the GI region and complete segregation of $V_o$ to the GB region. In all N_Rand configurations, where the Gd$^{3+}$ concentration is constant with depth, there is still a small increase in the concentration of $V_o$ per Å$^3$ at the GBs. Thus indicating that while the dopants strongly attract oxygen vacancies, there is still a contribution from the GB. If the GB structure was not a driving force for $V_o$ segregation, then we would have seen an equal or greater concentration of $V_o$ in the GI region of the N_Rand configurations. In effect, in the N_Rand configurations, the GB and the dopant Gd$^{3+}$ in the GI are in competition for oxygen vacancies.

The average cation-oxygen coordination number (CN) within the first coordination shell (3 Å from the cation) as a function of temperature (figures 8(C), (D)) show that Ce$^{4+}$ is surrounded by a greater number of oxygen ions on average compared to Gd$^{3+}$. This is a common feature within the GB structures, doping schemes and configurations studied. This is evidence that there is a stronger interaction between Gd$^{3+}$ and $V_o$ compared to Ce$^{4+}$ and $V_o$.

The formation of this first nearest neighbour Gd$^{3+}$ − $V_o$ clustering has been reported in the literature [37] for bulk cerium dioxide. For the N_Rand configurations, the oxygen CN of Ce$^{4+}$, either in the GI or in the GB,
decreases as the concentration of Gd$^{3+}$ increases from 10 to 30%. The oxygen CN of Ce$^{4+}$ in the GB region of N_GB configurations follows the same trend, although the difference between 10% and 16% Gd$^{3+}$ doping is less prominent. The same pattern applies to the oxygen CN of Gd$^{3+}$ in both N_Rand and N_GB configurations, which is due to the decrease of the total oxygen ions available in the simulation cells.

We also used residence time analysis, i.e. the average time spent by an oxygen atom within the first coordination sphere of a cation, to define the preferential affinity to oxygen with Ce$^{4+}$ or Gd$^{3+}$. On average, we find that oxygen resides longest closer to Ce$^{4+}$ than Gd$^{3+}$ (figures 8(A), (B)). This supports the stronger interaction between oxygen vacancies and Gd$^{3+}$. The residence time decreases with increasing temperature as

**Figure 6.** Time averaged 2D density profiles of the centre of mass of the cations (Ce$^{4+}$/Gd$^{3+}$) displayed every 0.5 ps at 2100 K for the stoichiometric and 16 GB Σ3(111) and Σ5(210) structures. The white dots denote the cation arrays parallel to the grain boundary plane. Patterns have been drawn to aid visibility.

**Figure 7.** Oxygen vacancy distribution within the grain interior (GI) and GB regions of each configuration at a representative temperature of 2100 K. The full dataset across the temperature range studied can be found in the SI.
the diffusion of oxygen becomes more predominant. At high temperature the residence time for both Ce$^{4+}$ and Gd$^{3+}$ converge to the same value. It is also evident from our data that all the GBs, i.e. extended defects, behave in a similar way, and have a marginal effect on the time oxygen resides close to a cation, i.e. for Gd$^{3+}$ a point defect.

Based upon these observations and our defect segregation energies (figure 4), we infer two key points. First, there is a strong interaction between Gd$^{3+}$ and V$_o$, which causes oxygen vacancies to distribute partially due to the distribution of the Gd$^{3+}$. This is not surprising given that the effective charges of Gd$^{3+}$ and V$_o$ are $-1$ and $+2$ respectively. Secondly, GBs themselves have a strong interaction with oxygen vacancies and cause some V$_o$ to segregate to the boundary despite uniform distributions of Gd$^{3+}$.

3.5. Oxygen diffusion at GBs

The presence of dopants was found to significantly increase the oxygen transport along the GB. We illustrate this by showing a typical 1 ns trajectory of 3 oxygen atoms (1 in the GB and two in the GI) for three different GB simulations, for example a time averaged density of diffusing species (oxygen) shows that in N_GB configurations, enhanced diffusion is localised to the GB, with no change in diffusion in the GI when compared with the stoichiometric structure (figures 9(A) and (B)). In contrast, in N_Rand configurations there is significant diffusion in both the GB and GI (figure 9(C)). Both observations can be rationalised by examining the oxygen vacancy distribution. N_Rand configurations have a more uniform distribution of V$_o$ albeit with a higher concentration in the GB, throughout the structure. This more even distribution of charge carriers facilitates diffusion throughout. In N_GB configurations V$_o$ have all localised in the GB leaving few hopping sites in the GI, as it is for stoichiometric configurations.

As the GI and the GB regions display such different behaviour, we treated the two regions separately. Considering the GB regions for all the GB configurations, our data does not show significant variation in the magnitude of the diffusivity (i.e. diffusion coefficient figures S6 and S7). As the concentration of Gd$^{3+}$ increases, the diffusivity increases for all configurations.

In the N_GB configurations (where all Gd$^{3+}$ are located in the GB) there is only a small concentration of oxygen vacancies in the GI. For this reason, the activation energies for V$_o$ diffusion could not be reliably calculated in the GI regions for these configurations due to a lack of statistics. However, activation energies were able to be calculated in the GI regions of the 10, 16 and 30 N_Rand configurations, and are 0.8, 0.9 and 1.0 eV respectively. GB regions generally have a slightly increased activation energy compared with the GI (figure 10). The $\Sigma_3$(111), $\Sigma_1$(311), $\Sigma_5$(210) and $\Sigma_9$(221) N_Rand configurations have a similar but slightly larger activation energy at the GB compared with the GI regions whereas the $\Sigma_5$(310) and $\Sigma_1$(331) N_Rand configurations have a much larger activation energy in the GI regions compared with the GB. With the exception...
of the $\Sigma 19(331)$ GB the N_Rand configurations have lower activation energies than the N_GB configurations. This highlights that the specific local microstructure of these materials can have a large effect on transport properties. This is in line with experimental predictions that GB regions reduce the conductivity of the material.

The stoichiometric $\Sigma 5(210)$ has the highest activation energy, followed by the stoichiometric $\Sigma 5(310)$, indicating that these GBs may be strongly blocking oxygen transport. However upon the introduction of dopants there is a large decrease in the Ea for both GBs to values similar to all other GBs.

A possible explanation for the low diffusivity in the $\Sigma 5$ boundaries relates to the cation density at the boundary compared with the interboundary region. We find in the stoichiometric $\Sigma 3$, $\Sigma 9$, $\Sigma 11$ and $\Sigma 19$ boundaries there is a slight decrease in cation density, whereas in the $\Sigma 5$ boundaries there is an increase in cation density (figure 11). Upon introduction of impurities there is a decrease in the cation density at the boundary due to a slight widening of the boundary region (figures 11(b), (c)). The contribution of the cation density at the GB
to the transport properties of boundaries provides a possible explanation for the strong blocking nature of the stoichiometric $\Sigma 5$.

3.6. Electrostatic potential at GBs
We have calculated the electrostatic potential as a function of distance either side ($-15$ to $+15$ Å) of the GB core positioned at 0 Å (figures 12, 13), for each GB within each scheme (stoichiometric CO, doped GB region (N_GB) and randomly doped GB and GI regions (N_Rand)). The lattice polarization is illustrated by the X projection of the mean electrostatic potential (figure 12—red dashed line). The sharp oscillations along X are due to the oppositely charged planes of Ce$^{4+}$/Gd$^{3+}$ and O$^{2-}$. The polarization field is seen more clearly from a running average of the electrostatic potential, calculated across a distance equal to one lattice spacing (figure 12—blue solid line). Generally there are quite substantial differences between the profiles of different GBs. Some structures show disruption of the electrostatic potential at the core of the GB that extend into the GI; this is hardly visible in the $\Sigma 5(111)$ whereas it is significant in the $\Sigma 5(310)$.

We find that N_GB configurations have a slightly lower potential at the boundary relative to the stoichiometric structures (figure 13), which is in contrast with the N_Rand configurations, which generally have

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Figure 11. Cation density difference between the grain interior region and the grain boundary region for all configurations studied (A). Time averaged two dimensional density profiles of the centre of mass of both Ce$^{4+}$ and Gd$^{3+}$ displayed every 0.5 ps at different temperatures, overlaid with the one dimensional cation density profile for the stoichiometric (B) and 16_GB GDC (C) $\Sigma 5(210)$. 
a slightly larger potential. This is due to the distribution of oxygen vacancies within the systems. The N_Rand configurations have a constant distribution of Gd$^{3+}$ throughout but an uneven distribution of V_o (i.e. the average V_o density is greater in the GI compared to the GB regions, figure 7), thus there is a greater net positive charge at the GB relative to the GI. In contrast the N_GB configurations display segregation of both Gd$^{3+}$ and almost all V_o at the GBs, thus there is a reduction in charge density at the GB region relative to the GI and so the potential is smaller (figure 13).

4. Discussion

We have demonstrated that we have a simple, robust approach for generating GB structures, with a high throughput computational approach by putting together all possible surface terminations, scanning each surface relative to the other and at each site performing an energy minimisation. In this way we have generated realistic models of ceria CSL tilt GBs, which are characteristic of the fluorite structure [31–34, 38–43].

All calculations, both molecular mechanics and MD, show that GBs are sinks for gadolinium and oxygen vacancy segregation (figures 4, 5 and 7), although the oxygen vacancies (V_o), segregation depends on GBs local structure. For example the Σ3(111) shows a small (0.06 eV) driving force for V_o segregation, whereas the Σ5 (310) has a larger segregation energy for V_o (up to 0.5 eV). This observation agrees with the findings of Dholabhai et al, where the defect energy is found to be sensitive to the local environment, i.e. the GB [18]. The segregation of V_o was also found to be dependent on distance from the GB core by Allen et al [44] to a depth of

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Figure 12. Red dashed lines: Poisson potentials calculated from molecular dynamics simulations as a function of distance from the grain boundary plane (−15− + 15 Å) at 2100 K for the stoichiometric, 10_GB and 10_Rand configurations. Blue solid lines: running average potentials over one lattice spacing.

Figure 13. Difference between the average electrostatic Poisson potential at the grain interior and at the grain boundary core for the stoichiometric CO (Blue), N_Rand (Orange) and N_GB (Green) configurations for all grain boundary structures.
approximately 1.5 nm. This is similar to that found from EELS, which revealed an enhanced oxygen vacancy and gadolinium concentration in first 2–4 nm from the GB and is assumed to be the effective width of the space charge layer \[1,3\]. For a information the reader can refer to more detailed papers \[12,20\].

A key result is that although GBs are sinks for oxygen vacancies, dopant segregation may play a much greater role in their segregation. All N_GB configurations, where all Gd\(^{3+}\) was segregated in the GB regions see a complete depletion of \(V_o\) in their GI regions (figure 4), which is in line with previous experimental reports \[12,45–47\]. Whereas in N_Rand configurations, where there is an equal amount of Gd\(^{3+}\) in the GI, a significant amount of oxygen vacancies do not segregate to the GB. We therefore speculate that as devices degrade over time and the Gd\(^{3+}\) concentration decreases in the GI and increases in the GBs, there will be a depletion of charge carriers in the GIs and thus an overall decrease in conductivity.

As there is accumulation of \(V_o\) in the GB, oxygen diffusion increases due to the increase of charge carriers. However, visual inspection has shown that this is limited to the GB region, hence the high oxygen diffusion remains parallel to the GB plane (figure 9). Although the oxygen diffusion in GB regions is much higher than in the GI regions, the activation energies are higher due to the energy required for an oxygen to leave the coordination sphere of an already undercoordinated cation atom. A higher activation energy for oxygen diffusion in GB was measured by Avila-Paredes et al, for heavily Gd doped \[48\]. The activation energies for oxygen in our GI regions (figure 4) are in line with experiments with heavily doped Gd samples (30%) having the highest Ea. As the dopant concentration decreases so does Ea \[49–52\]. We can comment on the blocking effect of GBs in GDC within the context of our results. Generally this blocking behaviour has been quantitatively described using the space charge layer model, which sees a positive electrostatic potential at the GB core due to segregation of oxygen vacancies and oxygen vacancy depletion (space charge layers SCL) adjacent to the core; this induces a reduction in ionic conductivity \[21,52–54\]. It is energetically favourable for large quantities of Gd\(^{3+}\) to segregate to the GB, along with the majority of charge carriers (\(V_o\)). This depletion of charge carriers in the GI results in the blocking effect of GBs as diffusion is limited to the GB planes (i.e. parallel to the GB plane). The simulated potential maps show this same behaviour for a number of GBs, i.e. with a positive core potential along with depletion zones.

Positive space charge potentials of 0.3 V have been obtained for polycrystalline ceria which is in good agreement with some of those calculated for our GBs \[55\]. Furthermore the blocking GB effects depend also on temperature and the dopant content and type \[56–58\]. When the temperature is high enough, the GB resistance appears to become negligible in comparison to the grain resistance, although this behaviour varies with dopant types and concentrations (usually 15 mol% regardless of the dopant type). Samples of heavily doped cerium oxides, prepared by Spark Plasma Sintering in the form of a high density (>98%) body with grain size of ~15 nm, showed no GB blocking effect and moreover the conductivity was demonstrated to be purely ionic \[10\].

5. Conclusions

We have conducted simulations on two different GDC systems, namely N_GB (i.e. dopants segregated at the GBs) which is an analogue for a degraded solid electrolyte of a SOFC device, and N_Rand (i.e. dopants randomly distributed between GBs and GIs) which is an analogue for a freshly made material. We find that segregation of Gd\(^{3+}\) to the GBs is a thermodynamically favourable process and thus the N_Rand configurations will degrade into the N_GB configurations over time. Furthermore, as the oxygen vacancies are strongly attracted to Gd\(^{3+}\) the resulting high concentrations of Gd_2O_3 at the N_GB GBs lead to a reduction in GI oxygen transport and this transport is limited to the GBs. Counter to this, we find that a more uniform distribution of Gd\(^{3+}\) allows transport to occur in the GIs as well as in the GBs as oxygen vacancies can also reside close to Gd\(^{3+}\) dopants in the GI. Thus segregation of dopants over time is a significant factor in the blocking effect of GBs in GDC, which we evaluated in terms of electrostatic potential.

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Author contributions

ARS and MM carried out the simulations, ARS performed the data analysis, MM and SCP designed the study, ARS and MM wrote the manuscript with contributions from all authors.

ORCID iDs

Adam R Symington  
https://orcid.org/0000-0001-6059-497X

Marco Molinari  
https://orcid.org/0000-0001-7144-6075

Stephen C Parker  
https://orcid.org/0000-0003-3804-0975

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