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Defect segregation facilitates oxygen transport at fluorite UO_2 grain boundaries

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An important challenge for modelling transport in materials for energy applications is that in most applications they are polycrystalline, and hence it is critical to understand the properties in the presence of grain boundaries. Moreover, most grain boundaries are not pristine stoichiometric interfaces and hence dopants are likely to play a significant role. In this paper, we describe our recent work on using atomistic molecular dynamics simulations to model the effect of doped grain boundaries on oxygen transport of fluorite structured UO_2 . UO_2 , much like other fluorite grain boundaries are found to be sinks for oxygen vacancy segregation relative to the grain interior, thus facilitating oxygen transport. Fission products further enhance diffusivity via strong interactions between the impurities and oxygen defects. Doping produces a striking structural alteration in the $\Sigma 5$ class of grain boundaries that enhances oxygen diffusivity even further. This article is part of the theme issue ‘Energy materials for a low carbon future’.

1. Introduction

As of 2018, 66% of the worlds energy is generated from coal, oil and gas, while solar/wind energy is responsible for less than 5% (figure 1) [1]. Rapid expansion of greener alternatives is a necessity in order to reduce the impact of global warming. Nuclear energy plays a vital role in twenty-first century energy production and is responsible for 11.1% of the worlds energy production. Nuclear energy is an established technology that has functioned across the globe for half a century and has the potential to bridge the gap between fossil fuel and renewable technologies for a low carbon future [2]. Despite the ubiquity of nuclear energy production, there are still many poorly understood aspects [3]. Uranium oxide (UO_2) is a common polycrystalline energymaterial used in nuclear energy, but it is challenging to work with due to its propensity for oxidation [3]. Ionic transport in polycrystalline materials is a common research question for many energy materials. In UO_2 understanding oxygen

transport is key to understanding the corrosion of the fuel. The fluorite lattice of UO_2 accommodates additional oxygen with little expansion up to around $\text{UO}_{2.5}$ stoichiometry but then undergoes a transition to a layered structure which is associated with a 36% volume increase [4,5]. In a nuclear power plant, this can cause swelling and eventually cracking of fuel rods, which can in turn release harmful contaminants into the environment [6]. Developing a fundamental understanding of oxygen transport properties in UO_2 can therefore be used to improve the efficiency, lifespan and, most importantly, safety of nuclear power plants.

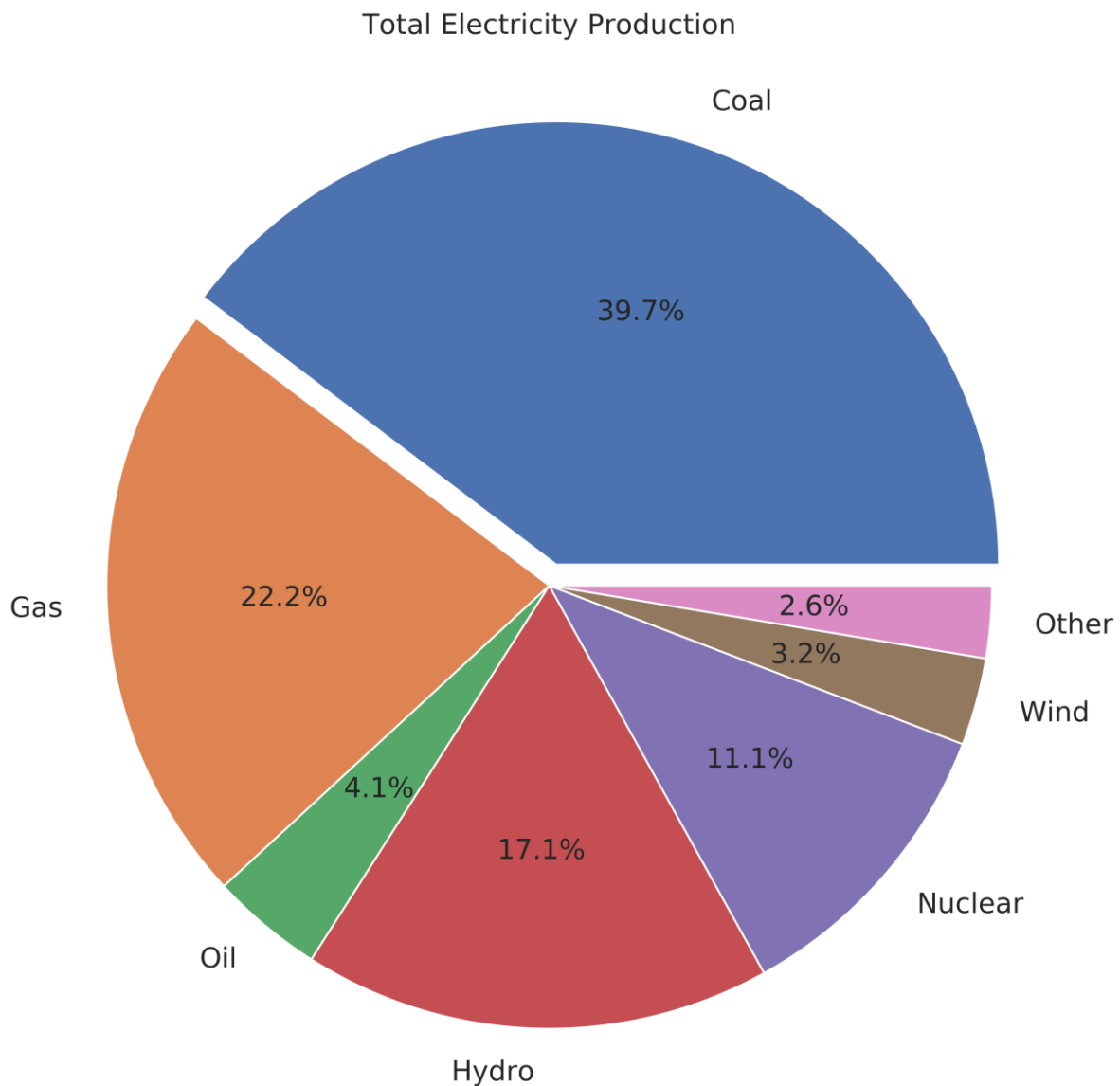


Figure 1. Total contributions to global energy production from coal, gas, oil, hydroelectric, nuclear, wind and other sources. The data were obtained from the global energy database [1].

Although oxygen transport and impurities are well documented in UO₂ [7–12], there is no work considering the two phenomena together. The transport properties of GBs have received some attention in recent years but the results have been contradictory. Using experimental techniques, Marin et al., and Sabioni et al. both reported no change in the oxygen transport properties at grain boundaries [7,13]. Whereas, using molecular dynamics studies, Verwerft et al. [14] and Arima et al. [15] both report enhanced oxygen transport at grain boundaries. The latter suggested that this effect was due to the misorientation angle of the grain boundaries.

Further molecular dynamics studies by Vincent-Aublant et al. and Williams et al. have found enhanced diffusion within the grain boundary region at the atomic scale [16,17]. Grain boundaries in other fluorite materials are well studied although there are contrasting interpretations. For example, there are studies stating that it is generally accepted that diffusion along grain boundaries is faster than in the bulk due to the higher defect concentrations and the reduced activation energy of oxygen hops [17,18]. Whereas other studies claim that there is no fast ion diffusion along grain boundaries [19,20]. Furthermore, grain boundaries have been shown to have a blocking effect to ionic transport across the boundary. This is considered to be due to the space charge effect, whereby segregation of charged defects to the grain boundary causes a reduction in ionic transport across the boundary [21–24].

Chemical impurities, i.e. non-stoichiometric cations and anions, are present in high concentrations within UO₂, particularly after time within a reactor [25]. Impurities can be introduced to the fuel in three common ways. Fuel fabrication, e.g. fuel pellet sintering. Iron cations are a common impurity, widely reported within UO₂ at high concentrations (100–180ppm [26]) and attributed to fuel pellet sintering with steel equipment at high temperatures 1750 °C [13,26–36]. A second common way for impurities to enter UO₂ is as a fuel poison, e.g. gadolinium, which is a common UO₂ dopant, acting as a burnable poison to control the reactivity of fuels in boiling water reactors [37–41]. Gd₂O₃-doped UO₂ has recently been investigated computationally and found to significantly increase the oxygen diffusivity of bulk UO₂ [42], furthermore, Th-doped UO₂ has also been studied and found to have higher diffusivity [43]. The most common defects are fission products, which are produced during the burning of UO₂. There are a wide variety of fission products, and they can be grouped into four categories based upon their chemical state. They can exist as volatile fission products (Kr, Xe, Br, I); metallic precipitates (alloys); ceramic precipitates (oxides based on Rb, Cs, Ba, Zr, Nb, Mo, Te) and oxides dissolved in the fuel (Sr, Zr, Nb, Y, La, Ce, Pr, Nd, Pm, Sm) [44].

There is significant evidence, both experimental and theoretical, which shows that impurities segregate to UO₂ grain boundaries [25,45] as well as other fluorite boundaries [46]. Hiernaut

et al. found that fuel oxidation enhanced the segregation of non-soluble fission products from the bulk to the boundaries [47]. Insoluble fission gases such as Xe migrate to grain boundaries where they form bubbles [48,49], Xe can undergo further chain decay leading to other stable fission products, e.g. La/Gd³⁺ has been shown to segregate to the grain boundaries, resulting in an increase in oxygen conductivity [50]. Recognizing the potential significance of this in this work, we investigate the combination of chemical impurities (fission products and fabrication impurities) within extended structural defects (grain boundaries) and the effect that this combination has on the oxygen transport properties of UO₂.

Despite the importance of grain boundaries (GBs) and fission products, their combined effect on the oxygen transport properties of UO₂ remains poorly understood and a number of important questions remain. Using large-scale molecular dynamics (MD), we explore the effects of some common impurities (M=M³⁺, Gd³⁺ and La³⁺) on the oxygen diffusivity at grain boundaries in UO₂, and we discuss our findings within the broader context of the literature.

2. Methodology

This work employs a classical potential model throughout, derived by Molinari et al. [51] and Williams et al. [17] in the fashion of Pedone et al. [52]. The model is based on rigid ions and uses partial charges (electronic supplementary material, table S1). This model has been shown to accurately reproduce the structural and elastic properties of UO₂ [17]. All molecular mechanics calculations, and all models of grain boundaries were generated using the METADISE [53] code as described in detail elsewhere [17,54].

All molecular dynamics simulations (MD) are performed using the DLPOLY code [55]. MD simulations of 5 ns were completed using a timestep of 1 fs with supercells of 8000 species (further information in electronic supplementary material, table S2) and an 8.5Å cut-off. Equilibration was performed using the NPT ensemble until unit cell volume had been converged. Production simulations were carried out within a temperature range of 2000–3000K at intervals of 250K using the NVT ensemble with a Nose–Hoover thermostat. Cation impurities (Fe³⁺, Gd³⁺ and La³⁺) were substituted onto uranium lattice sites up to a concentration of 1% and were distributed randomly within the grain boundary region (figure 2). This low concentration was chosen to establish whether even a small concentration of dopants will affect oxygen transport, i.e. early stage of corrosion. All details on models are included in electronic supplementary material, table S2. These models are constructed under the approximation that impurities segregate at the boundary as suggested by experimentation [56,57]. Oxygen vacancies were introduced randomly to maintain charge

neutrality throughout the entire structure. Oxygen vacancies reached their equilibrium distribution within the NPT MD simulation, this was confirmed by examining the

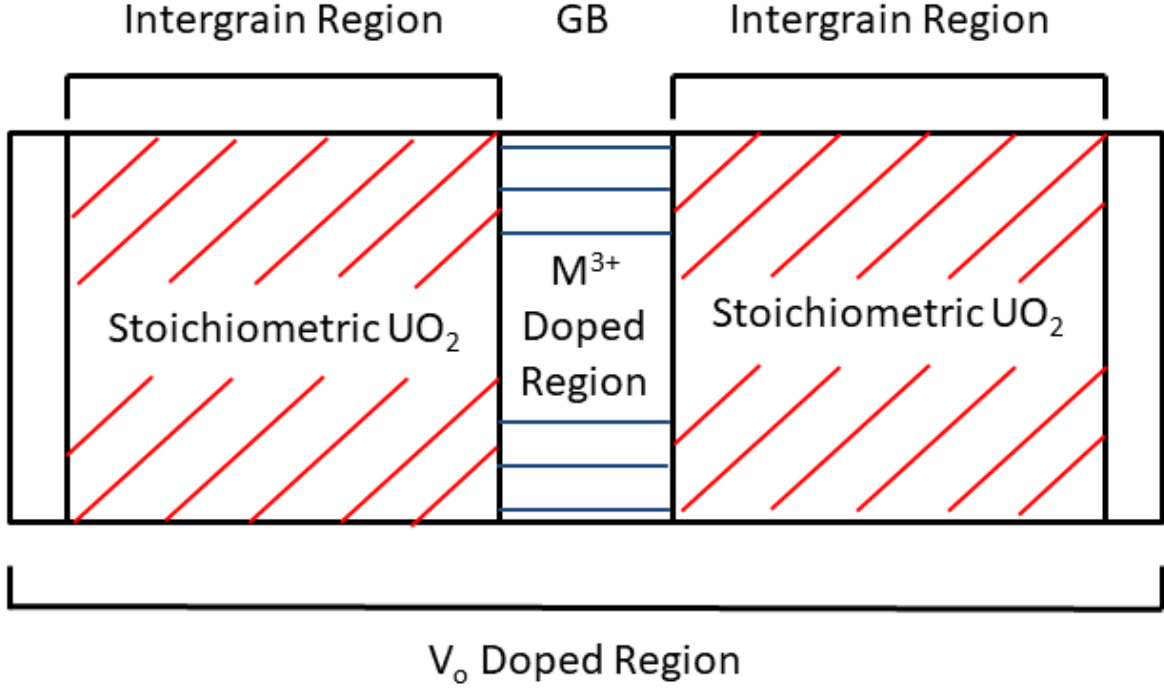


Figure 2. Schematic illustrating the model configuration for grain boundary and doping scheme.

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. Tracer-diffusion data for O within grain boundaries was obtained from a regional mean squared displacement (MSD) within the grain boundary according to

$$\langle r_i^2(t) \rangle = 6D_0t, \quad (2.1)$$

where $\langle r_i^2(t) \rangle$ is the MSD, D_0 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 grain boundary region.

We use the residence time τ to evaluate the average length of time that an oxygen atom spends in contact with each cation (U⁴⁺ and M³⁺). The τ was calculated from the residence time correlations function, which is defined as

$$\langle R(t) \rangle = \left\langle \frac{1}{N_0} \sum_{i=1}^{N_t} \theta_i(0)\theta_i(t) \right\rangle, \quad (2.2)$$

where N is the number of oxygen atoms within a 3\AA 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\AA radius at t and 0 otherwise. An oxygen atom was only considered to have left the 3\AA radius if it did so for at least 2 ps, which allowed molecules that temporarily left then re-entered to be included in τ . Equation (2.2) is integrated to calculate τ .

$$\tau_r = \int_0^{\infty} R(t) dt. \quad (2.3)$$

3. Results

(a) Potential surfaces of grain boundaries

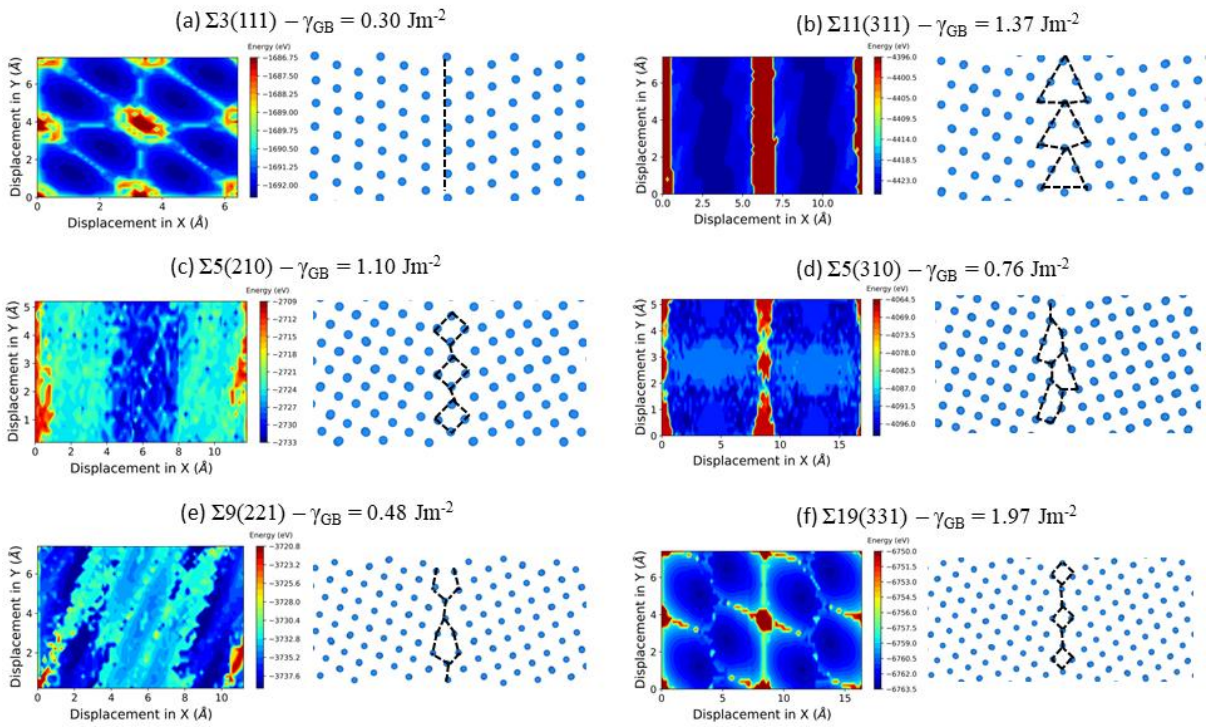


Figure 3. Potential energy surfaces for all grain boundaries (blue and red areas represent low and high energy GB structures) along with their lowest energy structure (only U atoms (blue) shown for clarity) and the grain boundary formation energy.

The $\Sigma 3(111)$, $\Sigma 11(311)$, $\Sigma 5(210)$, $\Sigma 5(310)$, $\Sigma 9(221)$ and $\Sigma 19(331)$ tilt grain boundary configurations have been constructed according to coincidence site lattice theory [58]. The potential energy surface was probed as a function of displacements of one grain relative to the other in the fashion of Galmarini et al. [54,59]. A two-dimensional grid of energies was constructed to map the complexity of the grain boundary structure. At each point of the grid, a full minimization was carried out and the grain boundary formation energy σ_{GB} was calculated using

$$\gamma_{GB} = E_{GB} - E_{Bulk} / 2A \quad (3.1)$$

where E_{GB} and E_{Bulk} are the energies of the grain boundary configuration and the UO₂ bulk simulation cells, respectively, and A is the GB area. A gradient colour map for each boundary is presented in figure 3, where low and high energy grain boundary configurations are highlighted in the blue and red areas; the structures of the lowest energy configurations are also presented for each grain boundary.

The lowest energy grain boundary structures for the $\Sigma 3(111)$, $\Sigma 5(210)$, $\Sigma 5(310)$, $\Sigma 9(221)$ and $\Sigma 11(311)$, show strong resemblance to experimental structures of CeO₂, and doped ZrO₂ [56,60,61]. The low σ_{GB} values of the $\Sigma 3$ and $\Sigma 9$ boundaries indicate the presence of high concentrations of these boundaries in UO₂ polycrystals in line with experimental SEM analysis of UO₂ samples [62].

(b) Grain boundary doped structure

As molecular mechanics calculations do not account explicitly for temperature effects, we have simulated all the lowest energy structures in figure 3 within the molecular dynamics framework. These were first annealed at high temperature and the structures are all consistent with previous calculations [17]. All stoichiometric structures were then doped following the doping scheme illustrated in figure 2. We have also considered a case wherein all impurities are located within the intergrain region of the structure and calculated the energy difference in order to confirm that segregation is energetically feasible. All energy differences are negative, showing that segregation is energetically feasible (figure 4). Doping does not cause any significant structural change with increasing temperature in the $\Sigma 3(111)$, $\Sigma 9(221)$, $\Sigma 19(331)$ and $\Sigma 11(311)$ boundaries. By contrast, the presence of impurities promotes an alteration to the structure of the $\Sigma 5(210)$ grain boundary and a partial structural

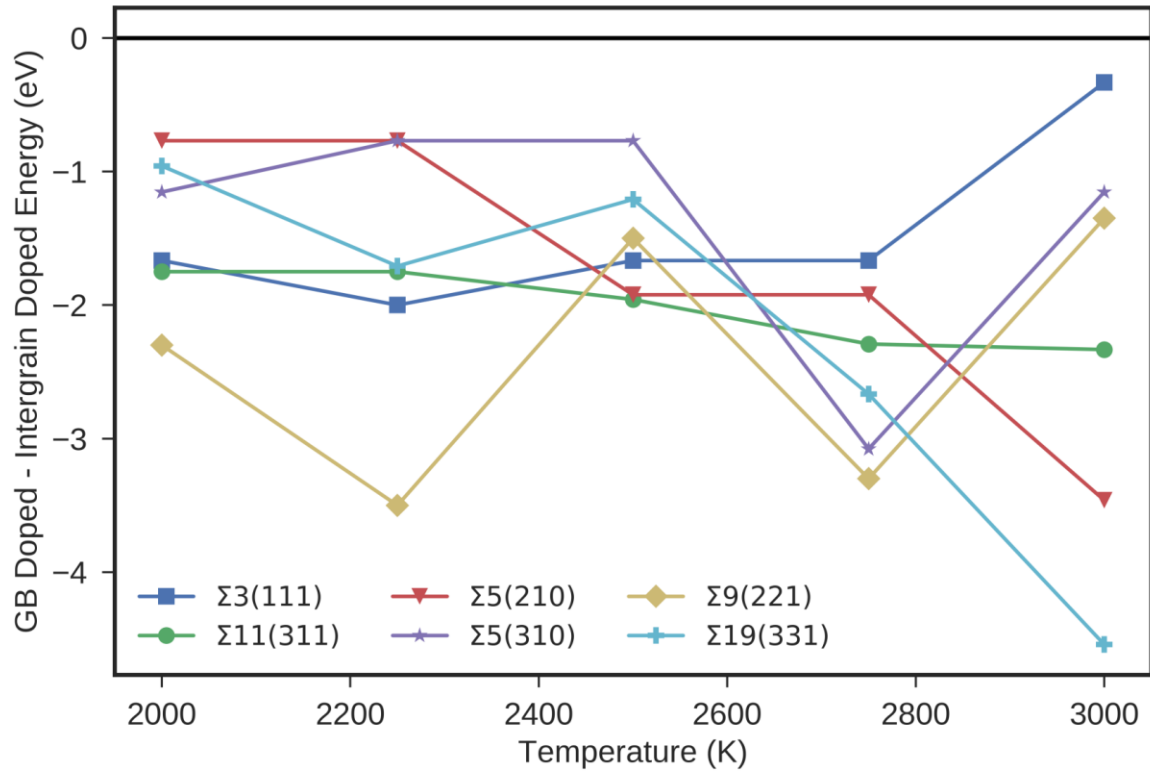


Figure 4. Energy difference between dopants in the doped GB structure and doped IG structure, calculated by subtracting the energy of the intergrain region doped structure from that of the GB-doped structure.

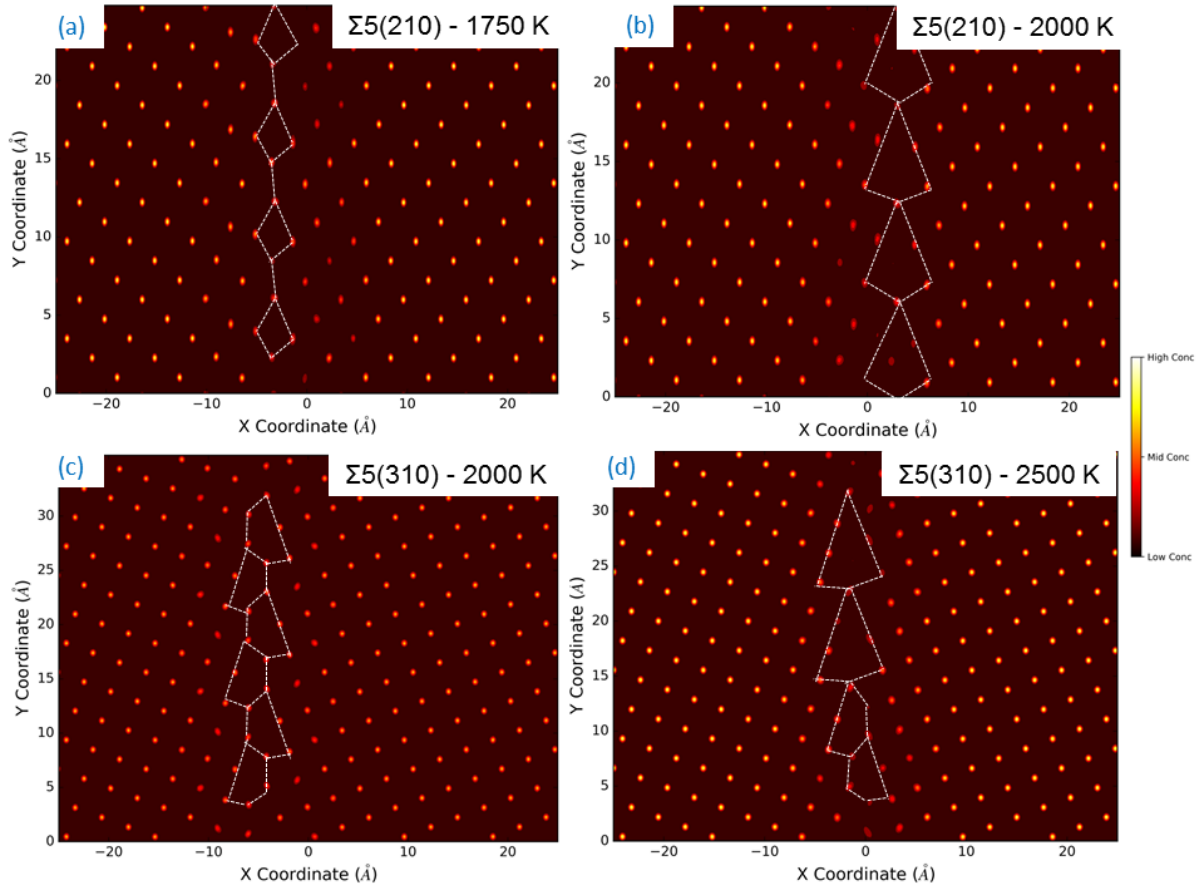


Figure 5. (a,b) Time averaged two-dimensional density profiles of the centre of mass of the cations ($U_{4+}/M_{3+}Q_1$) displayed every 0.5 ps at different temperatures for a 1% Fe_{3+} -doped $\Sigma 5(210)$ and (c,d) $\Sigma 5(310)$ grain boundaries. The red dots denote the U arrays parallel to the grain boundary plane. Patterns have been drawn to aid visibility.

change in the $\Sigma 5(310)$ grain boundary. Figure 5 depicts the time averaged two-dimensional density profiles of the centre of mass of the cations (U_{4+}/M_{3+}) in the $\Sigma 5$ grain boundaries at different temperatures. A structural change has been previously reported in the $\Sigma 5(210)$ GB in stoichiometric UO_2 and occurs within a temperature range of 2400–2600K [17]; when the structure is doped the transition occurs between 1700 and 2000 K. In the $\Sigma 5(310)$, the partial structural change occurs above 2500K for the doped boundary but it has not been reported in the case of stoichiometric UO_2 .

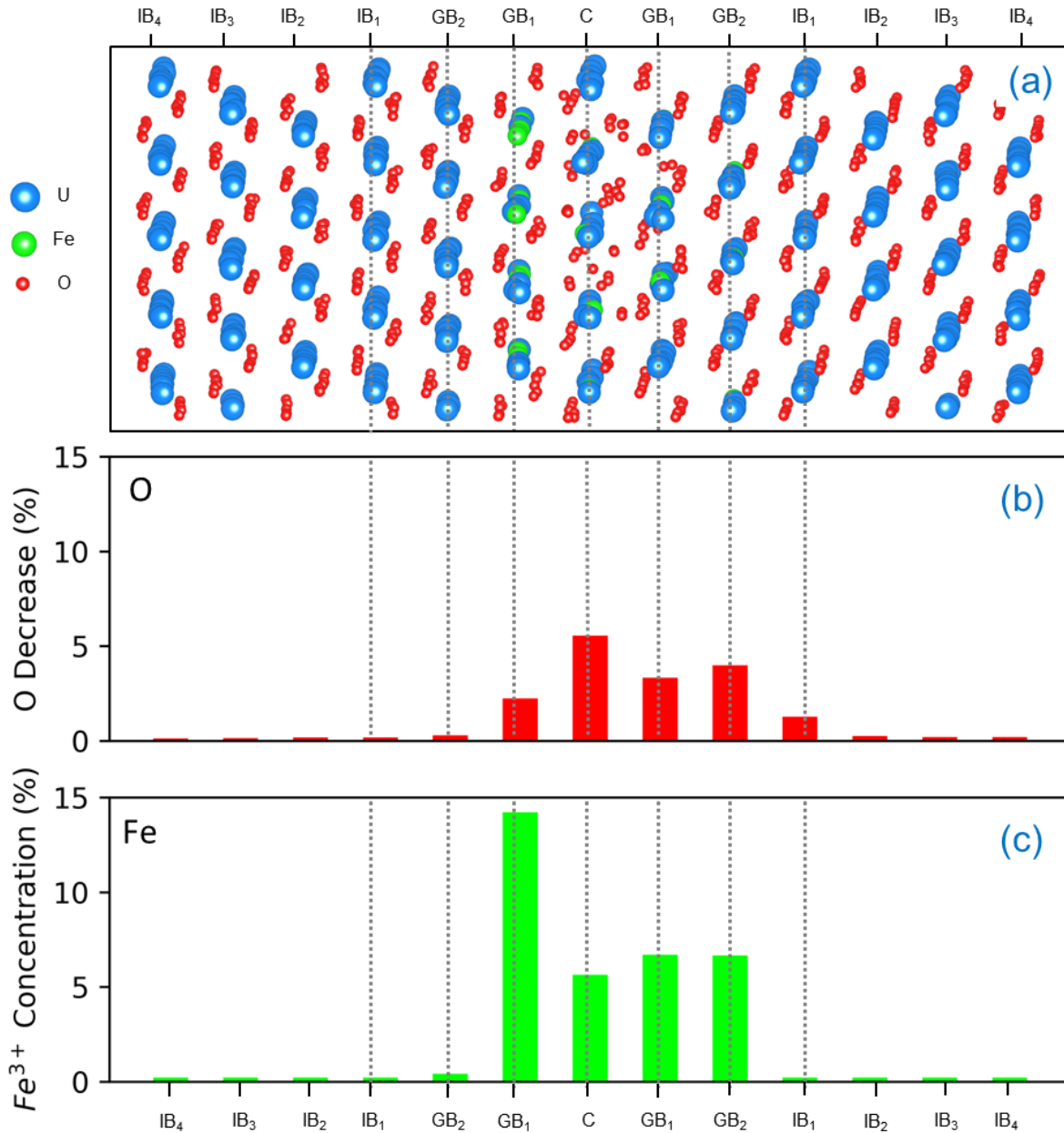


Figure 6. (a) Atomic configuration of Fe-doped $\Sigma 3(111)$ along $[110]$ direction. (b) Percentage concentration of oxygen vacancies per UO_2 layer relative to the stoichiometric structure. (c) Percentage concentration of Fe^{3+} cation per UO_2 layer relative to the stoichiometric structure. For clarity, IB, GB and C refer to UO_2 layers in the interboundary region, within the grain boundary width and the grain boundary core, respectively.

The energy map for the two $\Sigma 5$ boundaries is relatively complicated with many structural configurations within the low energy areas (figure 3). These structural changes as a function of temperature show that impurities stabilize metastable grain boundary configurations, which may not be accessible at low temperature when the structure is stoichiometric.

(c) Oxygen vacancy segregation

Oxygen vacancies were randomly distributed throughout the entire system (figure 2). During the NPT MD simulations which are mobile species, reached their equilibrium position within the doped structure. To quantify the segregation of segregation within the doped grain boundary region, we have evaluated reduction in oxygen concentration for all grain boundaries. As their Q2 behaviour in each boundary is similar, here we present the reduction in oxygen concentration (figure 6b) and Fe distribution (figure 6c) in the grain boundary region compared to the grain interior for the 1% Fe³⁺-doped $\Sigma 3(111)$ grain boundary (figure 6a). concentration of Fe³⁺ cation per UO₂ layer relative to the stoichiometric structure. For clarity, IB, GB and C refer to UO₂ layers in the interboundary region, within the grain boundary width and the grain boundary core, respectively.

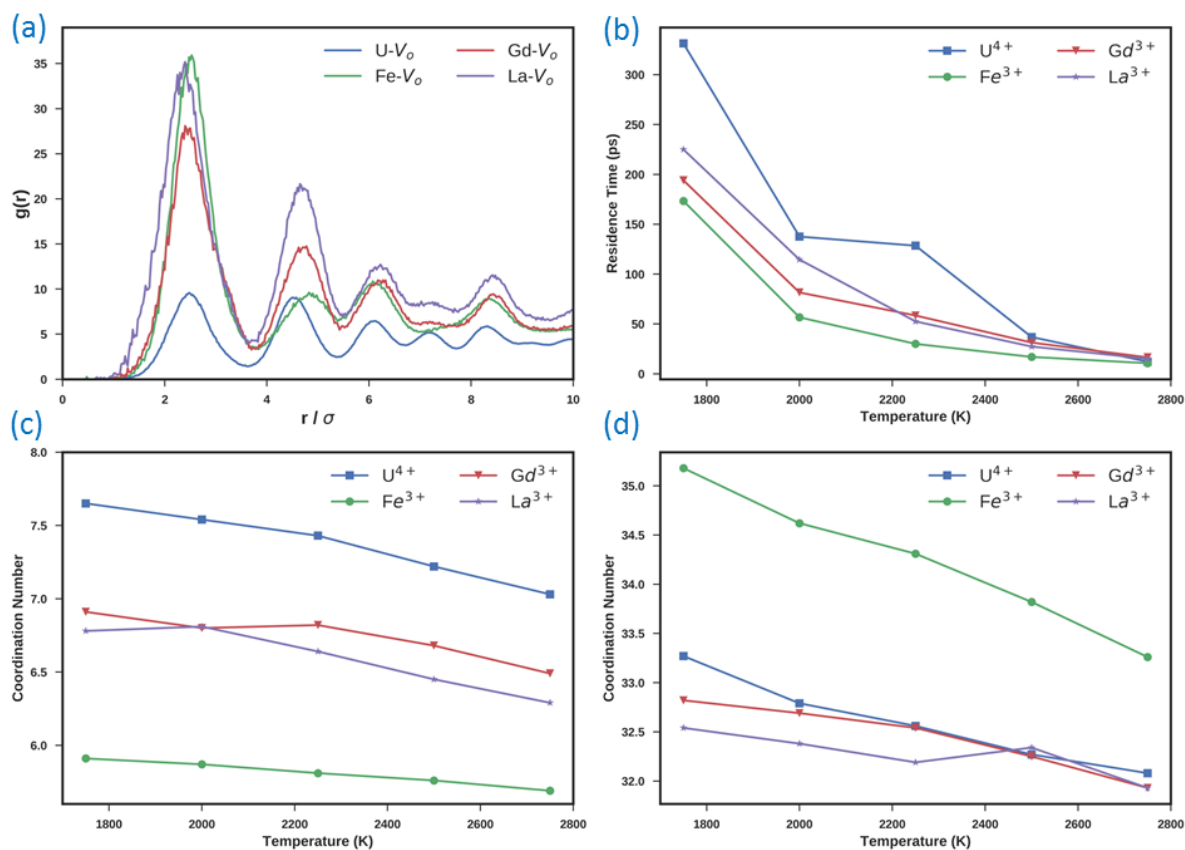


Figure 7. (a) Radial distribution functions for U^{4+} , Fe^{3+} , Gd^{3+} and La^{3+} (blue, green, red and purple lines) atoms within the grain boundary region with oxygen vacancies for the $\Sigma 3(111)$ GB. (b–d) Residence time, coordination number in the first (0–3 Å) and second (3–6 Å) shells for oxygen with U^{4+} (blue squares), Fe^{3+} (green circles), Gd^{3+} (red triangles) and La^{3+} Q1 (purple stars) cations as a function temperature in the $\Sigma 3(111)$ boundary.

The radial distribution functions of cation (figure 7a) were calculated in the fashion of Lucid et al. [63] and provide evidence that the M^{3+} increases greatly at short distance (i.e. for the nearest neighbours) for all the M^{3+} compared to the U^{4+} . This is evidence that V_o interact strongly with the impurity compared to the host uranium lattice. Further inspection of the peaks of the radial distribution functions show that in contrast to Fe, La and Gd have also a second intense peak, which is evidence that for these two dopants the interaction with the vacancy is extended to the next-nearest neighbour positions. M^{3+} defect clusters have been observed experimentally in other M_2O_3 -doped UO_2 [64]. This has also been seen for doped CeO_2 and linked to the difference in ionic radii of the dopants La^{3+} , Gd^{3+} , Fe^{3+} (1.061, 0.958, 0.645 Å, respectively) compared to the host cation U^{4+} (0.89 Å) [65].

We used residence time analysis, i.e. the average time spent by an oxygen atom within the coordination sphere of a cation impurity at the boundaries. We find that oxygen resides longest close to U^{4+} then $La^{3+} > Gd^{3+} > Fe^{3+}$ (figure 7b) which again follows the atomic radii of the impurity cations. The average coordination number within the first coordination shell (0–3Å from the impurity) and second coordination shell (3–6Å from the impurity) are shown in figure 7c,d. Fe^{3+} in particular has a significantly lower average CN within the first coordination shell. By contrast, Fe has a higher average CN within the second shell, which supports the RDF data which suggest that oxygen vacancies reside within 3Å of the Fe but up to 6Å for Gd and La. The percentage increase in V_o concentration within the grain boundary region of each structure is presented as a function of temperature (figure 8). There is a common behaviour for our grain boundaries considered, whereby there is an increase in V_o concentration in the grain boundary region. The $\Sigma 5(310)$, $\Sigma 9(221)$, $\Sigma 19(331)$ and $\Sigma 11(311)$ boundaries show a 1.5–2.5% increase in vacancy concentration in the full grain boundary region regardless of the type of impurity up to a temperature of 2750 K, where the oxygen sublattice becomes significantly mobile.

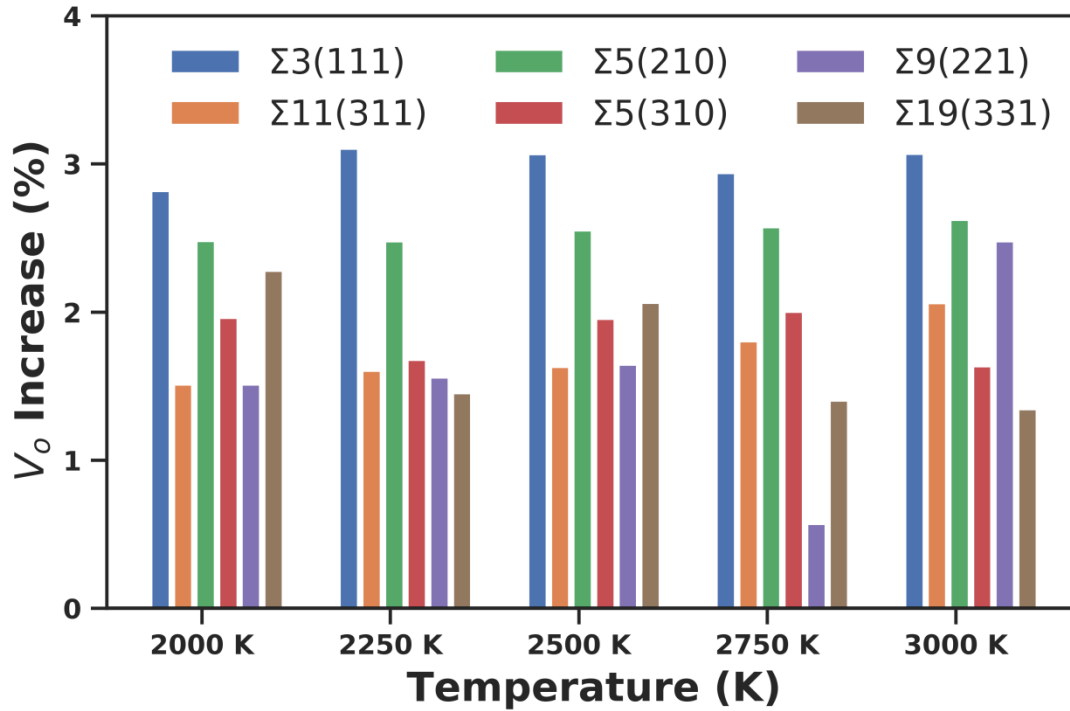


Figure 8. Oxygen vacancy concentration within each grain boundary between 2000 and 3000 K.

To separate the effects of the grain boundary and the impurities, we compared the oxygen stoichiometry of the stoichiometric structures with that of the IG-doped structures mentioned in figure 4 and found no change in the oxygen concentration at the boundary. This indicates that it is the impurities driving the segregation behaviour in UO_2 . V_o segregation at grain boundaries is generally accepted for fluorite structures, e.g. Gadolinium-doped ceria (GDC) and Yttria stabilized zirconia (YSZ), in line with the space charge theory [23]. In this work, we have only considered the segregation behaviour of oxygen vacancies at grain boundaries and we have not calculated the electrostatic potential and the space charge effect. Arora & Aidhy [66] studied the energetics of V_o within UO_2 grain boundaries and found vacancy segregation favourable when compared to the bulk material. Several other studies have reported within doped grain boundary systems [67–71]. This represents the first time that impurity promoted oxygen vacancy segregation at the grain boundaries has been proposed in UO_2 .

(d) Oxygen diffusion at grain boundaries

Our modelling results show that impurities significantly increase the oxygen transport within the grain boundaries. A simple visual representation is shown in figure 9 where a single GB oxygen atom over a 1 ns trajectory is depicted in grey for a stoichiometric (figure 9a) and 1% Fe^{3+} -doped (figure 9b) grain boundary. This shows that there is localization of the

oxygen diffusing species only in the grain boundary region, thus the grain boundaries act as a sink for vacancies. This behaviour is consistent with other studies investigating the effect of space charge on transport [24].

The oxygen diffusion coefficients are shown in electronic supplementary material, figure S1 for all the grain boundary configurations. We find that the diffusion enhancement in stoichiometric boundaries follows the order $\Sigma 3(111) > \Sigma 9(221) > \Sigma 19(331) > \Sigma 11(311) > \Sigma 5(310) > \Sigma 5(210)$ at a representative temperature of 2500 K. There is a significant difference in the diffusion coefficient of the grain boundaries, with a 1 order of magnitude difference between the lowest value of $0.049 \times 10^{-9} \text{ ms}^{-2}$ obtained for the $\Sigma 5(210)$ and the highest value of $0.53 \times 10^{-9} \text{ ms}^{-2}$ found for the $\Sigma 3(111)$ at 2500 K. Impurity cations further increase the diffusion within the grain boundary with Fe^{3+} having a greater effect than La^{3+} and Gd^{3+} . The increase corresponds to $0.1 \times 10^{-9} \text{ ms}^{-2}$ for the $\Sigma 3(111)$, $\Sigma 9(221)$, $\Sigma 19(331)$, $\Sigma 11(311)$ boundaries and $0.5 \times 10^{-9} \text{ ms}^{-2}$ for the $\Sigma 5(210)$ and $\Sigma 5(310)$ boundaries. The large increase in the $\Sigma 5$ series is due to the $\Sigma 5$ structural changes discussed in §3a (figure 10).

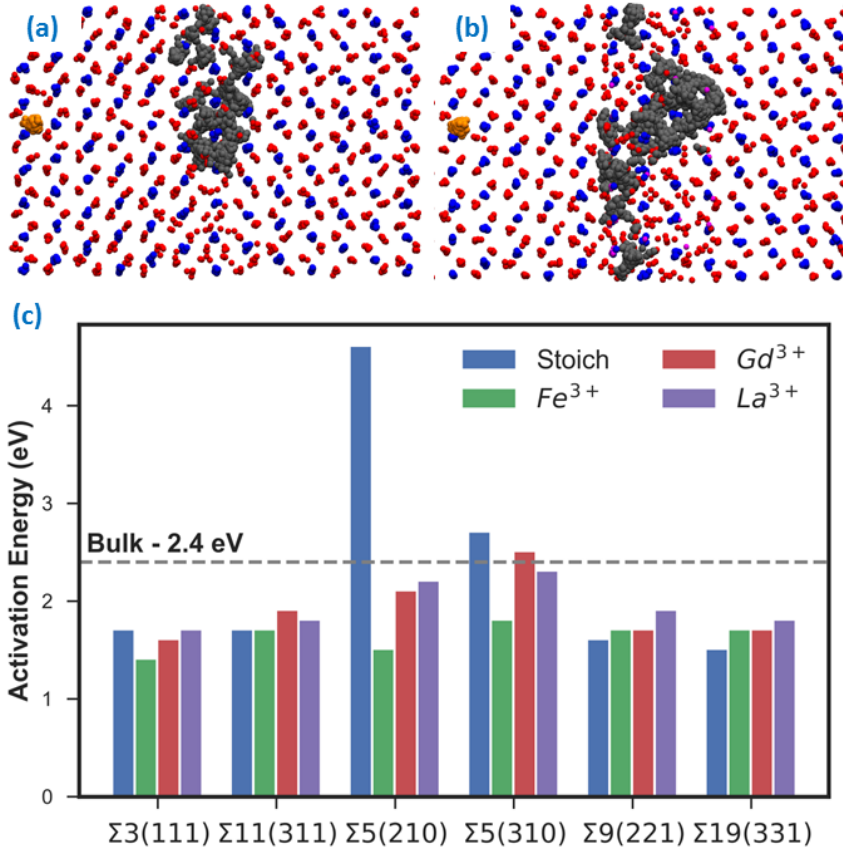


Figure 9. (a,b) Structure of the stoichiometric and 1% Fe^{3+} -doped $\Sigma 3(111)$ grain boundary structures. For clarity, oxygen, uranium and iron atoms are shown in red, blue and pink, respectively. To illustrate the effect of the grain boundary on diffusion, the full trajectory

across 1 ns for a single oxygen atom has been shown for a grain boundary oxygen (grey) and an interboundary oxygen (orange). (c) Activation energies for the stoichiometric (blue), Fe³⁺ (green), Gd³⁺ (red) and La³⁺ (purple) doped grain boundary regions compared to the activation energy of oxygen Q1 diffusion in 1% M³⁺-doped bulk UO₂ (2.4 eV).

The calculated activation energy for a 1% concentration of M³⁺-doped bulk UO₂ is 2.4 eV. While this is the activation energy of a UO_{2-x} system and a comparison should be treated with caution, the activation energy of stoichiometric UO₂ calculated experimentally –2.60 eV should be noted [72]. For clarity, we only present activation energies for oxygen diffusion within the grain boundary region (figure 9c). There is a general decrease in activation energy (E_a) from the stoichiometric bulk (2.4 eV) to the grain boundaries with the exception of the $\Sigma 5(210)$ and $\Sigma 5(310)$ boundaries. The stoichiometric $\Sigma 3(111)/\Sigma 11(311)$ and $\Sigma 9(221)/\Sigma 19(331)$ boundaries have similar E_a –1.7 and 1.6 eV, which is approximately half that of the intergrain region. Fe³⁺ and Gd³⁺ cause a small decrease in E_a in the $\Sigma 3(111)$ boundary, while La³⁺ has no effect. With the exception of Fe³⁺ in the $\Sigma 11(311)$ boundary, impurities cause a small increase in E_a in the $\Sigma 9(221)$, $\Sigma 19(331)$ and $\Sigma 11(311)$ grain boundaries compared to their stoichiometric counterparts. So while the impurities are promoting increased diffusivity, the activation energy is for the most part unchanged or slightly increased. For the stoichiometric $\Sigma 5$ boundaries, there is a particularly high E_a , 4.3 and 2.7 eV for the $\Sigma 5(210)$ and $\Sigma 5(310)$, respectively, highlighting the poor transport properties of these boundaries.

This shows that the $\Sigma 5$ boundaries are blocking oxygen transport. Upon the introduction of impurities, there is a large decrease in the E_a for both the $\Sigma 5(210)$ boundary and a modest decrease for the $\Sigma 5(310)$ boundary, which we infer is due to the structural change discussed in §3a. In our previous work, we reported modest increases in transport in small segments of the $\Sigma 5$ boundaries at short timescales. This work highlights that at long timescales when considering the boundary as a single structure, there is a blocking effect.

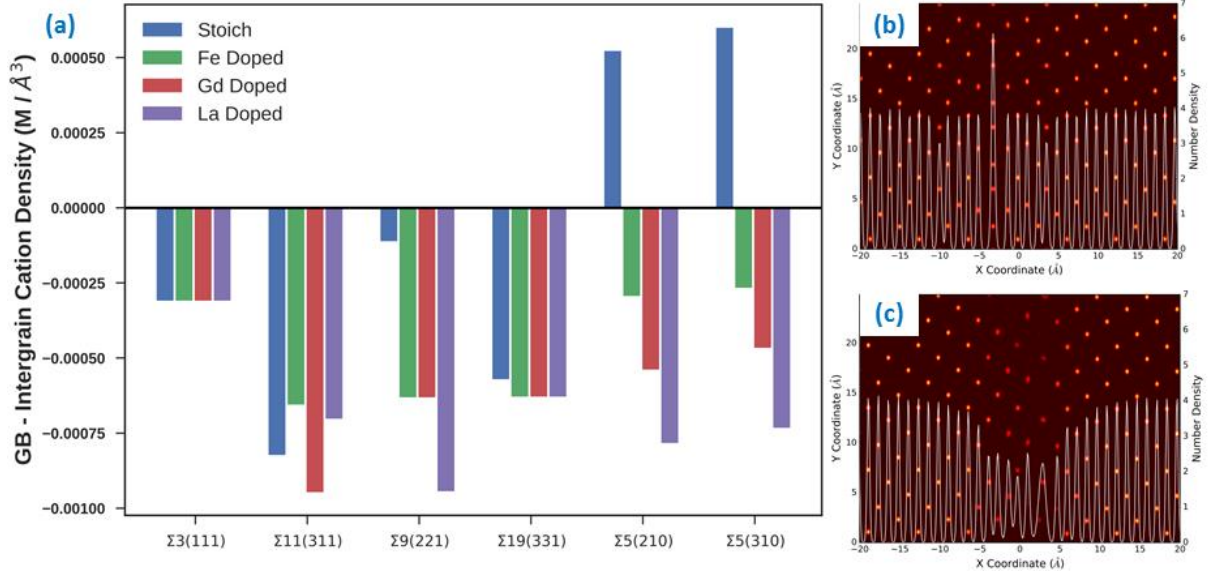


Figure 10. Cation density difference between the intergrain region and the grain boundary region a). Time averaged two dimensional density profiles of the centre of mass of both U and M3+ displayed every 0.5 ps at different temperatures, overlaid with the one-dimensional uranium density profile for the stoichiometric (b) and 1% Fe doped (c) $\Sigma 5(210)$.

A possible explanation for the low diffusivity in the $\Sigma 5$ boundaries relates to the cation density at the boundary compared with the inter-boundary region. Upon going from the interboundary region to the grain boundary in the $\Sigma 3$, $\Sigma 9$, $\Sigma 11$ 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 10). Upon introduction of impurities, there is a decrease in the cation density at the boundary due to a small increase in grain boundary width (figure 10c). Relating the cation density at the grain boundary to the transport properties of boundaries provides a possible explanation for the blocking nature of the $\Sigma 5$.

4. Discussion

We studied the early stage of segregation of impurities at grain boundaries, and we demonstrated that even at a concentration as low as 1%, there is segregation of oxygen vacancies and an increase of local oxygen diffusion that will impact the oxygen storage capacity of the fuel and so the availability of oxygen to enter the corrosion process. Our results demonstrate that the impurity content of UO_2 can have important implications for the corrosion of nuclear material. Our work illustrates the importance of the pre reactor stage of the fuel cycle. Fe^{3+} is a potentially avoidable impurity that is found in all fuels as a result of the fuel pellet sintering. It has been shown that the amount of Fe within the fuel pellets can be reduced by different fabrication processes, e.g. high levels of Fe are characteristic of fuel produced by dry chemical conversion compared to other methods such as the water or gas flame methods [26]. Fabrication plants typically have a purity limit

(generally 1250ppm [73]). Given that impurities segregate to the grain boundaries [24,45], there will be high local concentrations of impurity within the grain boundaries, opposed to an homogeneous distribution of the impurity in the grain interiors. Based upon these results, sintering methods that minimize the inclusion of Fe within the UO₂ pellet are crucial to increasing the safety and lifetime of the fuel. Unlike Fe³⁺, our results add further evidence to previous experimental and theoretical studies that Gd³⁺ is enhancing the oxygen transport within the fuel and thus the corrosion. We have also provided information on the state of the grain boundaries within irradiated UO₂. The presence of La³⁺ in UO₂ is unavoidable as it forms through fission chain decay within the reactor [74]. These results show that La³⁺ will increase the corrosion through oxygen diffusion and in the case of the $\Sigma 5$ boundaries cause structural changes. Experimental studies of post reactor fuel should pay careful attention to La³⁺ concentration within the spent fuel as its presence could indicate unstable grain boundary systems.

These results can be expected to be applicable to the wider field of fluorite grain boundaries. While it is accepted that transport along grain boundaries is higher than bulk transport, transport across the grain boundaries is blocked by the space charge effect. The space charge effect is well documented in CeO_{2-x} and doped zirconia and is due to the segregation of charged defects to the grain boundary [22–24]. This causes a blocking effect of transport across the boundary. Our results show that the M³⁺ cations present at the boundary strongly attract oxygen vacancies (figures 6–8), pulling them to the boundary where they will remain trapped and facilitate high levels of oxygen transport along the boundary and thereby increase the rate of corrosion. Kubo et al. has seen a similar effect in UO₂ whereby at Gd³⁺ concentrations at or exceeding 10 wt%, a potential barrier for the migration of electron holes formed [50]. This suggests that this behaviour (i.e. segregation of oxygen vacancies at grain boundaries and high diffusion in the grain boundary region) is indeed common to the fluorite structure and thus cation independent, whether U, Ce, Zr. Space charge can be probed Q3 using molecular dynamics simulations by calculating the electrostatic potential from the atomic trajectories. This therefore presents an avenue for future study on this topic.

5. Conclusion

The atomistic effects of grain boundaries are important to fully understand the transport properties of UO₂. Enhancing our fundamental understanding of these interfaces and their influence on oxygen ion transport is crucial for the future optimization of new nuclear fuel materials. In this study, we have quantified this effect using large-scale MD simulations. Our results support three key features. A common feature of a grain boundary structure is the segregation of oxygen vacancies at grain boundary regions, promoted by the impurity cations.

Which is related to the energetic preference for impurities to have a lower oxygen coordination number. The presence of different sites at the grain boundary provides a way for the material to accommodate the strain induced by the impurities. This increase in charge carriers (oxygen vacancies) induces an enhanced oxygen diffusivity which is localized at the grain boundary regions. Finally, there are structural changes occurring as a function of temperature for $\Sigma 5$ grain boundaries, which are facilitated by the presence of impurities; as the potential energy surface of these boundaries is complex, the presence impurity lowers the grain boundary energy allowing more structural configurations to be explored during the molecular dynamics simulation.

Our modelling shows that GB are areas of fast ionic diffusion and thus may enhance corrosion. As the material starts corroding, oxygen enters via the grain boundaries and diffuses out into the individual grains and ultimately form higher oxide phases, which has been predicted previously [75]. Impurities within grain boundaries will, based upon our results increase this process and ultimately accelerate the degradation of the fuel.

Data accessibility. Force field parameters, atomic configurations, diffusion coefficients and Arrhenius plots can be found in the electronic supplementary material. Atomic density analysis and the mean squared displacements were carried out using the polypy code [76].

Authors' contributions. A.R.S. carried out the simulations, performed the data analysis and wrote the manuscript with contributions from all authors; S.C.P., M.M. and A.R.S. designed the study; M.M. and S.C.P. derived the force fields used in the study.

Competing interests. The authors declare that they have no competing interests.

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