Special quasirandom structures for gadolinia-doped ceria and related materials

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Gadolinia doped ceria in its doped or strained form is considered to be an electrolyte for solid oxide fuel cell applications. The simulation of the defect processes in these materials is complicated by the random distribution of the constituent atoms. We propose the use of the special quasirandom structure (SQS) approach as a computationally efficient way to describe the random nature of the local cation environment and the distribution of the oxygen vacancies. We have generated two 96-atom SQS cells describing 9% and 12% gadolinia doped ceria. These SQS cells are transferable and can be used to model related materials such as yttria stabilized zirconia. To demonstrate the applicability of the method we use density functional theory to investigate the influence of the local environment around a Y dopant in Y-codoped gadolinia doped ceria. It is energetically favourable if Y is not close to Gd or an oxygen vacancy. Moreover, Y–O bonds are found to be weaker than Gd–O bonds so that the conductivity of O ions is improved.

Introduction

A criterion for solid oxide fuel cells (SOFCs) to become economical is the operation in the intermediate temperature range (500–700 °C).1 However, this temperature range presents difficulties for the operation of traditional ceramic cathodes and electrolytes and requires materials with enhanced O diffusion.2 Numerous candidate oxides are being investigated for cathode and electrolyte applications for the next generation of intermediate temperature SOFCs (IT-SOFCs).3–8 The research community is looking for alternative ways to enhance the ionic transport, such as the formation of an interface between dissimilar oxides.9–15 For example, Barriocanal et al.13 have determined that in strained interfaces between SrTiO3 and yttria stabilized zirconia (YSZ) the ionic conductivity can be increased by eight orders of magnitude. Recent calculations using density functional theory (DFT) support the enhancement in ionic conductivity in YSZ/SrTiO3 interfaces but point towards a more moderate increase (up by about 3.5 orders of magnitude).15

Methodology

A. Special quasirandom structure generation

DFT methods often rely on the construction of supercells with periodic boundary conditions. The calculations are straightforward for ordered systems. However, for systems which display atomic disorder they can be more complicated. Using a brute force approach the disordered system can be described by constructing a large supercell and randomly inserting the cations (here Gd or Ce) on their sublattice. In practical terms this is not feasible for DFT calculations as large supercells are required to adequately reproduce the statistics of random alloys.

With the SQS approach it is possible to adequately mimic the statistics of a random alloy in a relatively small supercell.17–21 In essence, SQSs are specially designed small-unit-cell periodic structures that closely mimic the most relevant near neighbor
pair and multisite correlation functions of random substitutional alloys. Due to the atomistic nature of the SQS approach, a distribution of distinct local environments existing in real random alloys is maintained, which is essential for the present work.

B. DFT calculations

The Vienna *Ab initio* Simulation Package (VASP)\(^{22}\) is used to investigate how Y doping affects the oxygen vacancy diffusion in Ce\(_{26}\)Gd\(_6\)O\(_{61}\). The exchange correlation is treated in the generalized gradient approximation of the Perdew–Burke–Ernzerhof edition.\(^{23}\) Pseudopotentials generated by the projector augmented wave method\(^{24}\) are employed. Convergence is achieved with a Gamma-centred 3 \(\times\) 3 \(\times\) 3 k-mesh. Kr 4d\(^{10}\) and Xe are considered to be the core states of Ce and Gd, respectively. The experimental lattice constant of 5.423 Å for Ce\(_{0.8}\)Gd\(_{0.2}\)O\(_{1.9}\)\(^{25}\) is used in our calculations of the Ce\(_{26}\)Gd\(_6\)O\(_{61}\) SQS supercell.

The on-site coulomb interaction\(^{26}\) is taken into account for the localized Ce 4f and Gd 4f orbitals. There are many choices for \(U\) parameters of Ce 4f in different situations, so that a test is necessary for our specific case. The experiment shows that Gd-doped CeO\(_2\) is ferromagnetic at 5 K.\(^{27}\) Thus, not spin polarized and spin polarized calculations are performed for the \((U, J)\) candidates (5, 0),\(^{28,29}\) (6.1, 0),\(^{30}\) (6.7, 0.7),\(^{31}\) and (7, 0).\(^{32}\) Furthermore, the lattice constants and atomic positions are optimized with an energy cut-off of 520 eV to find out the effects of different \(U\) and \(J\) parameters.

Results and discussion

A. SQS structure

In essence Gd and Ce atoms can randomly occupy equivalent lattice sites in GDC. Consequently, the formation of oxygen vacancies will occur with a multitude of distinct local arrangements of the surrounding host cations. These arrangements will affect the formation and migration of the oxygen vacancies. The representation of the random alloy by a very large supercell and the random occupation of the cation sublattice with Gd and Ce atoms to mimic the random nature of GDC is a computationally intractable approach to study defect processes using DFT.

As the fcc cation and simple-cubic anion sublattices do not exchange species, the configurational problem can be greatly simplified to that of a binary system. Thus, the total energy of the system depends on two types of interatomic interactions: those between atoms on the same sublattice (cation–cation and anion–anion) and those between atoms on different sublattices (cation–anion). We have generated two 96-atom SQSs corresponding to the compositions Ce\(_{26}\)Gd\(_6\)O\(_{61}\) (or 9% gadolinia doped GDC) and Ce\(_{24}\)Gd\(_8\)O\(_{60}\) (or 12% gadolinia doped GDC).\(^{20}\) Table 1 gives the pair correlation functions of the 96-atom SQS structures that mimic random GDC compounds (nn = nearest neighbor).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Structure</th>
<th>Cation–cation</th>
<th>Anion–anion</th>
<th>Cation–anion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 nn</td>
<td>2 nn</td>
<td>3 nn</td>
</tr>
<tr>
<td>Ce(_{26})Gd(<em>6)O(</em>{61})</td>
<td>Random</td>
<td>0.391</td>
<td>0.391</td>
<td>0.391</td>
</tr>
<tr>
<td></td>
<td>SQS-96</td>
<td>0.396</td>
<td>0.417</td>
<td>0.375</td>
</tr>
<tr>
<td>Ce(_{24})Gd(<em>8)O(</em>{60})</td>
<td>Random</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
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<tr>
<td></td>
<td>SQS-96</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
</tbody>
</table>

\(^{a}\) For anion–anion interaction, two distinct 3 nn pairs exist depending on whether a cation sits in between the two anions.

Fig. 1 96-atom SQS corresponding to compositions (a) Ce\(_{26}\)Gd\(_6\)O\(_{61}\) (or 9% gadolinia doped GDC) and (b) Ce\(_{24}\)Gd\(_8\)O\(_{60}\) (or 12% gadolinia doped GDC). Red (large light gray) spheres represent the Ce ions, blue (large dark gray) spheres the Gd ions, green (small) spheres the O ions and dotted circles the O vacancies.

Ce\(_{26}\)Gd\(_6\)O\(_{61}\) (or 12% gadolinia doped GDC)\(^{20}\) Table 1 gives the pair correlation functions of the generated SQSs in comparison with those of the random alloy. It can be observed that both the nearest-neighbor intrasublattice and intersublattice pair correlation functions of the random GDC structure are accurately reproduced by the SQS. The SQSs are presented in Fig. 1 in their ideal, unrelaxed forms. In Fig. 2 we show the atomic shifts during the relaxation of Ce\(_{26}\)Gd\(_6\)O\(_{61}\) by black arrows. As expected, the largest shifts appear in the vicinity of the vacancies.

B. Ce\(_{26}\)Gd\(_6\)O\(_{61}\)

For comparison, we address in Fig. 3 the electronic structure of CeO\(_2\). The valence band is dominated by the O 2p states.
with considerable contributions of the Ce 4f states due to finite hybridization. In addition, the Ce 4f states give rise to a pronounced peak around 2.5 eV. Spin polarized calculations with different $U$ and $J$ parameter sets produce for Ce$_{26}$Gd$_6$O$_{61}$ almost the same lattice parameters, band gap, and total energy as the not spin polarized one. The total DOS of the not spin polarized and spin polarized calculations with $U_{4f} = 5$ eV and $J_{4f} = 0$ eV for Ce is shown in Fig. 4. Neither spin splitting in the total DOS nor a magnetic moment is obtained. The experiment indicates that the remanent magnetization is very weak (in the order of $10^{-3}$ emu), where the ferromagnetism arises from the Ce$^{3+}$ and Gd$^{3+}$ ions.$^{27,33}$ However, the ferromagnetic ground state is not reproduced in the simulation because of the shortcomings of the ideal structure. Finally, we retain the spin polarized setting for all calculations to be consistent with the experimental determinations of ferromagnetism.

Comparing the results of different ($U$, $J$) sets for the Ce 4f orbitals, the lattice constants increase and are larger than the experimental value.$^{25}$ The band gaps are smaller than the experimental value of Gd-doped CeO$_2$ (Ce : Gd = 9 : 1), which is well known for DFT calculations. As the band gap almost does not vary for different Ce $U_{4f}$ and $J_{4f}$ parameters,
we choose $U_{4f} = 5 \text{ eV}$ and $J_{4f} = 0 \text{ eV}$ to obtain lattice constants which are closest to the experimental values. This parameter set has been widely used for CeO$_2$.28,29

The effect of $U$ and $J$ for Gd 4f orbitals is also investigated in spin polarized calculations with Ce $U_{4f} = 5 \text{ eV}$ and $J_{4f} = 0 \text{ eV}$. In fact, the lattice constants and band gap are little affected by the choice of the $(U, J)$ parameter set of Gd, because the concentration of doped Gd is not sufficient to dominate those properties. Gd $U_{4f} = 6.7 \text{ eV}$ and $J_{4f} = 0.7 \text{ eV}$ are taken for further investigation because they are well optimized as demonstrated in previous work.34 Some important parameters of the fully optimized structure are summarized in Table 2 to compare with experimental findings.

### Table 2: Crystal structure parameters and band gap of Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ after full relaxation with spin polarized calculations and Ce $U_{4f} = 5 \text{ eV}$, $J_{4f} = 0 \text{ eV}$, and Gd $U_{4f} = 6.7 \text{ eV}$, $J_{4f} = 0.7 \text{ eV}$ comparing with experiment

<table>
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<th></th>
<th>DFT calculation</th>
<th>Experiment</th>
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<tr>
<td>$a$ (Å)</td>
<td>5.547</td>
<td>5.426$^a$</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>5.548</td>
<td></td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>5.553</td>
<td></td>
</tr>
<tr>
<td>Angle</td>
<td>89.4 90.0 89.9</td>
<td>90$^a$</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>2.0</td>
<td>2.48$^b$</td>
</tr>
</tbody>
</table>

$^a$ Lattice parameters for Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$.25 $^b$ Band gap of Gd-doped CeO$_2$ (Gd : Ce = 1 : 9).27

Partial densities of states (PDOSs) of GDC are depicted in Fig. 5. The electronic structures of the six configurations are similar. We therefore address only the one with the lowest total energy in Fig. 6. The same group of atoms in GDC and Y-doped GDC is taken to plot the PDOS of Gd (Y), one O nn and the Ce connected by this O. In Fig. 5, the O 2p PDOS shows hybridization with the Gd 5d states from $-3.6 \text{ eV}$ to $-2.4 \text{ eV}$ and both with the Gd 5d and Ce 4f states from $-2.4 \text{ eV}$ to 0 eV and 2.1 eV to 2.7 eV. A similar picture is obtained in Fig. 6 for the PDOS in Y-doped GDC. However, as the arrows shown in Fig. 5(b) and 6(b) highlight, the hybridization with the Y 4d states is obviously not as strong as that with the Gd 5d states. Furthermore, the O 2p contributions from 2.1 eV to 2.7 eV in Fig. 6 are more pronounced than in Fig 5. In fact, the increased hybridization between the Ce 4f and O 2p states is related to the decrease in the Y–O hybridization. We conclude that the Y–O bonds are weaker than the Gd–O bonds, which supports our findings from the Bader analysis and the bond lengths.

**Fig. 5** PDOS of Ce 4f, Gd 5d, and O 2p in Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$. The arrow points at the difference between Gd–O and Y–O hybridization.

Total energy. This implies that the doping in experiments should be relatively uniform.

Using Bader analysis36 we compare the charge of Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ and Y-doped GDC. The O nn gains more charge from Y than from Gd after substitution. However, the charge of Ce and other O atoms almost does not change. All the 6 configurations show this charge increase which is around 0.03 in the O sphere. The increase indicates that the ionic nature of the bonds is enhanced and, therefore, that the covalency and strength are reduced. The Gd–O and Y–O bond lengths are also inspected. If the Gd–O and Y–O bonds are of the same strength, Gd–O should be longer than Y–O because of a slightly larger radius of Gd. Nevertheless, the average Y–O bond length (2.465 Å) is larger than the average Gd–O bond length (2.461 Å), demonstrating that the Y–O bond is weaker than the Gd–O bond.
Conclusions

The present study aims to aid the community in unravelling the intricacies of defect processes in GDC and related materials such as YSZ using a computationally tractable methodology. In particular we propose two SQS cells to mimic the local pair correlation functions of GDC for two technologically important compositions. The use of these SQS structures will allow the implementation of DFT or other electronic structure calculations to investigate such systems in a realistic way. Importantly, as the SQS method is not a mean-field approach, the distribution of distinct local environments is preserved. The average of them corresponds to the random alloy. The results of our DFT calculations reveal that it is energetically favourable for the system when the Y is not close to other dopant atoms or oxygen vacancies. Our Bader analysis shows that O gains more charge from Y than from Gd, so that the covalent bond is weakened. The Y–O bond length is slightly longer than the Gd–O bond length and the obtained PDOSs illustrate that the Y 4d and O 2p hybridization is weaker than the Gd 5d and O 2p hybridization. These two findings demonstrate that the Y–O bonds are weaker than the Gd–O bonds. Hence, the substitution of Gd by Y in GDC is expected to improve the conductivity of $O_2^\text{2+}/C_0$.

An enhancement of the ionic conductivity in Gd$^{3+}$ and Y$^{3+}$ codoped ceria as compared to singly Gd$^{3+}$ or Y$^{3+}$ doped ceria has been reported in ref. 37 and is fully in line with the picture derived from our calculations.

Acknowledgements

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References


Fig. 6 PDOS of Ce 4f, Y 4d, and O 2p in the most energy favorable Y-doped Ce$_{26}$Gd$_6$O$_{61}$ structure. The arrow points at the difference between Gd–O and Y–O hybridization.