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Interpreting oxygen vacancy migration mechanisms in oxides using the layered structure motif

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ABSTRACT

The manner in which oxygen vacancies migrate in oxide ceramics is analyzed in terms of an atom layer stacking motif to elucidate similarities and differences in migration mechanisms as a function of crystal structure and chemistry. In particular, five oxide structures are examined: rocksalt, spinel, bixbyite, pyrochlore, and fluorite. While there are similarities that are related to structure in the types of migration mechanisms that are possible, there are significant differences as a consequence of chemistry and deviations from the parent structures (rocksalt and fluorite). One primary difference occurs because of structural relaxations related to the complex chemistry in spinel and pyrochlore, in which oxygen ions tend to form localized groupings within which oxygen vacancy hopping mechanisms are particularly fast. While these mechanisms cannot lead to net migration, a kinetic Monte Carlo model does show that they do influence overall diffusivity. We conclude that the atom layer stacking motif is an effective scheme to understand the dependency of oxygen vacancy migration mechanisms on oxide crystal structure.

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1. Introduction

Oxide ceramics are a critical component of many technologies, from solid oxide fuel cells [1] to nuclear fuels and waste forms [2,3] to dielectrics in semiconductor devices [4]. In many of these applications, the mobility of ionic defects, particularly anion defects, the key factor determining the suitability of the oxide for that application. For example, solid oxide fuel cells and fast ion conductors function precisely because of the mobility of anions within the lattice [5].

Atomistic simulations can provide important details regarding the properties of defects in these materials [6]. Such simulations have revealed that interstitial clusters in MgO and UO₂ have high mobilities [7,8], that cation Frenkel pair recombination in pyrochlores always leads to antisite formation [9–11], and that, in AB₂O₄ spinel, B cation diffusion occurs via a vacancy mechanism on the A sublattice [12]. However, even the most sophisticated simulations must still be interpreted and placed into context for insight to be gained. This is particularly true in complex materials, where simply reporting mechanisms does not necessarily provide an understanding that is transferrable to other situations nor the

generalizations that highlight commonalities and differences between, for example, related but different crystal structures.

Here, we use atomistic simulations to examine the mechanisms responsible for doubly charged oxygen vacancy migration in a series of materials that vary in relative oxygen-to-metal content but are structurally related. In particular, we consider rocksalt and spinel, spinel being structurally related to rocksalt, and fluorite along with two fluorite-derivative structures, specifically bixbyite and pyrochlore. Upon irradiation, spinel can transform into a disordered rocksalt structure [13], while both bixbyite and pyrochlore transform into disordered fluorite structures [14,15]. We interpret the migration mechanisms in terms of an atom layer stacking model recently developed by Sickafus et al. [16]. By comparing the behavior of oxygen vacancies in these compounds, we elucidate similarities and differences in oxygen vacancy migration mechanisms that depend on the structure and chemistry of these compounds.

2. Methodology

We use temperature accelerated dynamics (TAD) [17] along with pair potentials to examine the migration mechanisms of oxygen vacancies in a variety of oxide compounds. The use of TAD eliminates any bias in assumed mechanisms, because a molecular dynamics (MD) trajectory is used to discover pathways

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dynamically. Once an event has been identified, the nudged elastic band (NEB) [18] method is used to characterize the event by finding the relevant saddle point. Depending on the compound, these simulations are performed with a low temperature of between 600 and 2000 K for simulation times ranging from nanoseconds to 0.1 ms (no attempt was made to optimize parameters for a given system).

We chose to examine five different oxide structures – rocksalt, spinel, fluorite, bixbyite, and pyrochlore – which vary in stoichiometry between rocksalt and fluorite as illustrated in Fig. 1. Rocksalt and fluorite were chosen as they are the simplest compounds with integer oxygen/metal (O/M) ratios. The spinel structure is related to that of rocksalt while both bixbyite and pyrochlore are fluorite derivatives. Thus, choosing these compounds allows us to examine how the basic crystal structure of two families of compounds, as well as the complexities involved with deviations from integer stoichiometry, influence oxygen vacancy mobility. The specific chemical compounds simulated were MgO, MgAl₂O₄, CeO₂, Er₂O₃, and Dy₂Ti₂O₇. The interatomic interactions were described with a standard Buckingham potential [19] with long-range Coulomb interactions calculated using Ewald summation [20]. The potential parameters for these different compounds were taken from the literature. For MgO, we used the parameter set by Lewis and Catlow [21]. For MgAl₂O₄, we used the parameter set reported by Smith et al. [22]. We used the parameters of Vyas et al. [23] for CeO₂ and those of Kittiratanawasin et al. [24] for Er₂O₃. Finally, for Dy₂Ti₂O₇, we used the parameter set developed by Stanek et al. [25]. While we expect the barriers we report for various migration mechanisms to be dependent on the parameter set used, we also expect the basic physical trends to be well captured by these potentials. We note that these are fixed charge models and thus the vacancy always has the same charge state, formally +2.

All simulations were conducted using periodic boundary conditions. The cell size was typically the minimum possible size satisfying the minimum-image convention for a potential cutoff of 8 Å. This led to simulation sizes of 511 atoms for rocksalt, 447 atoms for spinel, 639 atoms for bixbyite, 703 atoms for pyrochlore, and 767 atoms for fluorite. These numbers account for the missing atom resulting from the creation of the oxygen vacancy.

Many of the results reported here are based on previous simulations in which, typically, we provided the value for the energy barrier of the rate limiting process for migration of the oxygen vacancy in the given compound, but did not elaborate any further on the actual pathways or alternative mechanisms. In particular, we reported migration barriers for the oxygen vacancy in MgO [26], spinel [27], Er₂O₃ [24], and pyrochlore [28]. Further, the behavior of the oxygen vacancy in Er₂O₃ was examined in detail by Kittiratanawasin and Smith [29].

3. Layered motif structure of oxides

The structure of oxides, particularly complex oxides containing more than 2 species, can be analyzed in a variety of ways. One common approach is to visualize the polyhedra that comprise the structure [30]. Topology has also been a powerful way to understand the structure of complex oxides [31]. More recently,

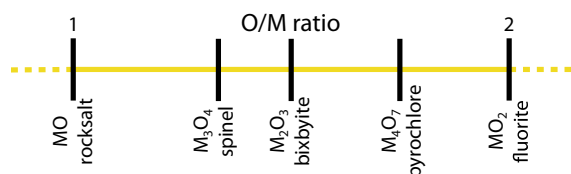


Fig. 1. Relationship between the five oxide compounds examined along an oxidation line scaled by relative oxygen/metal ratio.

Sickafus and colleagues have examined the structure of oxides from the point of view of an atom layer stacking model [16], building upon concepts originally proposed by Iida [32]. In this view of oxides, the atomic structure of a given compound is visualized as a series of atomic planes stacked in a [1 1 1] direction (for cubic compounds). Each of these planes exhibit particular arrangements of atoms that generalize across a wide range of oxide structures. These stacking motifs, illustrated in Fig. 2 for the compounds studied here, form the basis of each compound. It is simply the order in which they are stacked that governs the structure of the oxide.

The basic motif for rocksalt-based compounds (rocksalt and spinel) is alternating layers of metal (M) and oxygen (O). For fluorite and fluorite derivatives such as bixbyite and pyrochlore, the motif is O–M–O. The specific stacking sequences for rocksalt, spinel, bixbyite, pyrochlore, and fluorite are given in Table 1. In this view, the differences in structure between fluorite, pyrochlore and bixbyite are related to the individual structure of each layer. For example, in fluorite, all of the oxygen and metal layers are comprised of fully dense hexanets as illustrated in Fig. 2. In bixbyite, in contrast, the oxygen layers are not fully dense, but rather contain structural vacancies that accommodate the relative difference in stoichiometry between bixbyite and fluorite. In the case of bixbyite, these vacancies order in a very well defined pattern, referred to as a “wishbone kagome” structure (Fig. 2). Similarly, pyrochlore differs from fluorite in that half of the oxygen planes contain structural vacancies that form a “kagome” pattern. Pyrochlore has the extra complexity of having two different cationic species. These form fully dense planes of cations, but these planes alternate in chemistry, with some forming a kagome lattice of A cations with B cations filling the central hole of the kagome pattern, and others reversing the role of A and B cations (referred to as a “filled kagome pattern” in Fig. 2). Finally, spinel is related to rocksalt in that all of the oxygen layers are fully dense, but the metal layers alternate between a kagome pattern of B cations and a set of three quarter-dense planes of B–A–B cations, which together form a $\frac{3}{4}$ dense hexanet.

4. Migration mechanism of oxygen vacancies

Using the stacking motifs described above, we examine the migration mechanisms associated with oxygen vacancies as revealed by the TAD simulations. The goal is to identify both commonalities between the different compounds as well as differences and relate these to the stacking layers that comprise each material.

4.1. Rocksalt and spinel

4.1.1. Rocksalt

A schematic of the rocksalt structure is shown in Fig. 3. In this and all other schematics, the position of the ions are in their ideal positions and do not account for any structural relaxation. Spinel [33] and pyrochlore [34], in particular, are well known to have structural relaxations that can be described by positional parameters of the ions. While these relaxations do influence the barriers of the various migration mechanisms, for simplicity they are not included in the schematics.

Rocksalt, being possibly the simplest oxide, exhibits very straightforward mechanisms for oxygen vacancy migration. Viewed within the layer stacking motif, an oxygen vacancy can simply hop to any of the 6 nearest neighbors within the plane with equal probability. For MgO, the barrier governing this processes is 2.04 eV. There are equivalent mechanisms in the intersecting {111} planes, leading to a total of 12 symmetrically equivalent pathways for oxygen vacancy migration.

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