



Chemical expansion affected oxygen vacancy stability in different oxide structures from first principles calculations



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ABSTRACT

We study the chemical expansion for neutral and charged oxygen vacancies in fluorite, rocksalt, perovskite and pyrochlores materials using first principles calculations. We show that the neutral oxygen vacancy leads to lattice expansion whereas the charged vacancy leads to lattice contraction. In addition, we show that there is a window of strain within which an oxygen vacancy is stable; beyond that range, the vacancy can become unstable. Using $\text{CeO}_2/\text{ZrO}_2$ interface structure as an example, we show that the concentration of oxygen vacancies can be manipulated via strain, and the vacancies can be preferentially stabilized. These results could serve as guiding principles in predicting oxygen vacancy stability in strained systems and in the design of vacancy stabilized materials.

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1. Introduction

Oxygen vacancies have emerged as one of the key ingredients in a variety of materials' phenomenon both of fundamental and technological interests. Besides acting as charge carriers in the conventional ion-transport electrochemical processes [1,2] such as in oxygen sensors, electrodes and cathodes for solid oxide fuel cells [3], and in memristive devices [4,5], they have found growing appreciation in the emerging field of transition-metal oxides responsible for magnetic, orbital, electronic and transport properties [6,7]. There are also reports of high-temperature superconductivity induced by ordered oxygen vacancies [8]. In addition, the oxygen vacancies are found to act as healing agents in materials under radiation environments, thus paving ways for the design of better radiation tolerant materials for nuclear applications and radioactive waste storage [9].

In almost all of these fields, tailoring of interfaces in materials is being actively pursued as a design parameter to quantitatively enhance the properties [10]. For example, in the case of ion-transport, there are now multiple examples from both experiments and computation that show enhanced oxygen conductivity in interfacial materials as compared to bulk materials [11]. Similarly, recent

experimental results have demonstrated that interfaces act as strong sinks for radiation-induced point defects, thus increasing a material's radiation tolerance [12,13]. Multiferroicity and two-dimensional electron gas (2DEGs) heterostructures are other recent examples where materials' interfacing is being heavily exploited [14,15].

Oxygen vacancies are common to all these interfacial oxide materials and are either inherently present during synthesis or deposition, or are extrinsically created by adding dopants. Interfacial materials and materials that are used under extreme conditions are often strained. The strain in interfacial materials is due to lattice mismatch between two materials, while the strain in bulk materials could be due to temperature or chemical gradients, such as in nuclear reactor environments. Under such conditions, the behavior of oxygen vacancies, both kinetics and thermodynamics, is far from that in the bulk. In pursuit of gaining precise control over oxygen vacancies such that strain could be used as a 'knob' to preferentially functionalize vacancies, advancing the understanding of strain-influenced properties of oxygen vacancies is currently one of the most important areas of research in the oxide community [16].

Substantial progress has been made in recent years on the strain-induced kinetic properties of oxygen vacancies triggered by a study that revealed eight orders of magnitude increase in oxygen conductivity originating at the interface in $\text{YSZ}/\text{SrTiO}_3$ [17]. Such high conductivity has yet to be reproduced by other groups; however, from other studies since then, an underlying theme has satisfactorily

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emerged that oxygen migration barriers can be controlled by interfacial strain, i.e., tensile strain lowers oxygen migration barrier due to stretching of the bonds [11,18]. In contrast, the strain-influenced thermodynamic properties of oxygen vacancies are less understood. In a series of papers on non-stoichiometric ceria, the concept of chemical expansion, i.e., expansion or contraction of the lattice dimensions due to the presence of oxygen vacancies has been explored using both experiments and computation [19–22]. It was shown that oxygen vacancies lead to lattice expansion, and hence increase in lattice volume. A similar study on perovskite CaMnO_3 using density functional theory (DFT) calculations also showed that oxygen vacancy formation energy decreases under tensile strain conditions compared to equilibrium bulk, i.e., volume expansion induced by tensile strain stabilizes oxygen vacancies [23]. To develop more in-depth understanding, a much wider exploration across various oxide structure types is required to establish the thermodynamic stability of oxygen vacancies under strained conditions. In an effort to explore this concept in chemically and crystallographically different materials, we investigate the strain-induced oxygen vacancy stability of charged and neutral vacancies in rock-salt, fluorite, perovskite and pyrochlores based oxides materials using DFT calculations. We show that for a given material there is a window of strain within which an oxygen vacancy is stable; beyond that range, the vacancy can become unstable. Furthermore, we distinguish between *chemical expansion* of charged and neutral vacancies. The results demonstrate that neutral vacancies lead to lattice expansion; while in contrast, charged vacancies lead to lattice contraction, i.e., they are likely to be more stable under compressive strain. These results could serve as guiding principles in predicting oxygen vacancy stability in strained systems and in the design of vacancy stabilized materials.

2. Methodology

We perform DFT calculations using the VASP code [24]. In particular, the projector-augmented wave (PAW) method with plane waves up to the energy cutoff of 500 eV is used, and the exchange–correlation energy is evaluated by generalized-gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional [25]. All relaxations were done until the forces were smaller than 0.01 eV/Å. We simulate ten systems, i.e., CeO_2 , MgO , CaO , BaO , CaTiO_3 , SrTiO_3 , BaTiO_3 , $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Hf}_2\text{O}_7$. Recent research has established that the strong on-site Coulombic interaction needs to be corrected for CeO_2 . The Hubbard U -correction is applied to Ce 4f electrons as proposed by Dudarev et al. [26] using a value of $U_{\text{eff}} = 5$ eV based on the previous works [27]. For Ti and Hf, we found that the oxygen vacancy effects on lattice expansion are independent of the U -correction; therefore, we have not used the correction for the two atoms. All systems are modeled using their $2 \times 2 \times 2$ supercell. In each of these systems, charged and neutral oxygen vacancy is modeled using the Brillouin zone sampled with a $2 \times 2 \times 2$ Monkhorst–pack mesh k -points grid. Spin polarization is taken in account in all calculations. After the tests for plane-wave energy cutoff and k -point sampling, the numerical error is found to be less than 1 meV/atom, illustrating energy convergence for supercell size and k -points. The bulk lattice parameters obtained for all systems are within 2% of the experimental lattice constants.

3. Results

3.1. Oxygen vacancy stability in an interface structure

We first present an example of oxygen vacancy stability across an interface structure formed between fluorite-based CeO_2 and

ZrO_2 . The interface calculations are performed to show that the stability of the oxygen vacancy can be manipulated by applied strain. The supercell contains $1 \times 2 \times 12$ unit cells (288 atoms) in total, in which $1 \times 2 \times 4$ unit cell of ZrO_2 are sandwiched between $1 \times 2 \times 8$ unit cells of CeO_2 . Both materials are interfaced using (001) terminations sharing oxygen plane of atoms. The structure is fully relaxed using DFT and the final structure is used as the input structure for oxygen vacancy calculations. An oxygen vacancy is created by removing an oxygen atom from inside CeO_2 and from the interface in separate calculations. The oxygen vacancy image distance in the y direction is 2 lattice parameters (~ 11.06 Å); whereas in the x direction, it is 1 lattice parameter (~ 5.41 Å). While the image distance in x is relatively small, we tested our calculations by doubling the supercell in the x direction to a total of 576 atoms and did not find any significant difference in the relative energy/stability of the oxygen vacancy. Since we plot the oxygen vacancy stability relative to the interface (see Fig. 1a), the image interaction is expected to cancel out. (Here, the oxygen vacancy stability is defined as system energy containing oxygen vacancy in CeO_2 compared to that at the interface). Due to this reason and the high computational cost associated with the 576 atoms supercell, we chose to perform our simulations on the 288 atoms supercell. After full relaxation, the cell is then equally strained in the x and y directions that form the interfacial plane, and the system energy is calculated as a function of strain. The stability of oxygen vacancy inside CeO_2 (shown in square symbols) relative to that at the interface (in diamonds) is shown in Fig. 1a. In the unstrained case, the oxygen vacancy is more stable inside CeO_2 by 0.25 eV. Upon compression, the stability of the vacancy starts to change, and the vacancy is almost equally stable in CeO_2 and at the interface. On the tensile side, we see a similar, but gradual effect. Whereas the vacancy is stable in CeO_2 at up to 3% strain, as shown in Fig. 1a, the stability gradually decreases with increasing tensile strain. Eventually, at larger tensile strains, the stability will reverse similar to that in the compressed case. These simulations show that oxygen vacancies could be functionalized with the applied strain, and their stabilities can be desirably manipulated.

This stability behavior can be understood and to some extent predicted by a simple model using bulk single crystal. Here, we perform single crystal DFT calculations on a $2 \times 2 \times 2$ supercell bulk CeO_2 , where the supercell is hydrostatically strained and the total energy of the system containing a vacancy is followed. This energy profile (or vacancy stability) relative to the unstrained case is shown in Fig. 1b and is obtained using Eq. (1).

$$\Delta E^{s,v} = E^{s,v} - E^{0,v} \quad (1)$$

Here, $\Delta E^{s,v}$ is the change in the system energy containing a single vacancy at a given strain, s , $E^{s,v}$ is the total energy of the strained system, and $E^{0,v}$ is the total energy of the unstrained system. We also plot the energy profile of the system without a vacancy, i.e., equation-of-state as shown by red diamonds. As observed in Fig. 1b, the minimum energy for a system containing a vacancy is observed not at the equilibrium lattice parameter, i.e., at 0; instead it occurs under tensile strain revealing expansion of the lattice by the oxygen vacancy, thus stabilizing the vacancy under larger volume. The depth in the parabola is representative of the volume change caused by the oxygen vacancy. Further tensile strain, however, destabilizes the vacancy as shown by the parabolic nature of the curve demonstrating that the vacancy is stable only within a certain range of tensile strain. This is similar to the trend observed above for the interface structure, where the vacancy is only stable within a certain window of strain, particularly on the tensile side. Similar discussion on other interface structures and oxygen stabilities can be found elsewhere [28].

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