Interstitial and substitutional zirconium in SrTiO₃

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ABSTRACT

We investigate Zr in SrTiO₃ (STO) as a model for nuclear waste forms in which the fission product ^{90}Sr eventually decays to stable Zr through beta emission. The transformation of a divalent into a tetravalent constituent is expected to affect the long-term structural and chemical stability of this solid. Computational methods of electronic structure theory, specifically the density functional theory (DFT) within the supercell model, are used to predict the thermodynamic stability and electronic states of interstitial and Sr- or Ti-substituted Zr atoms in the STO lattice. Native defects such as vacancies and antisites are also considered. When Zr replaces Sr, its most stable configuration is to simply occupy the Sr site. For Zr added to the lattice, its most stable configuration is to replace a Ti, making a Zr_{Ti} impurity plus a Ti interstitial. Zr_{Sr} is predicted to be a double electron donor, Zr_{Ti} is electrically inactive and interstitial Zr and Ti are predicted to be quadruple donors, with all donor levels in the conduction band. The interstitials are all predicted to increase the crystal volume, and lead to a tetragonal distortion of the lattice. Experiments with injection of Zr and O atoms into STO qualitatively confirm these predictions of crystal structural changes.

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1. Introduction

Developing solid matrix materials for permanent disposal of high-level radioactive waste is a difficult scientific and technological challenge. Atomic structural damage and heating from the energy released in decay events and interaction with ambient oxygen or water may possibly compromise long-term confinement. While damage may anneal over time, heat may be conducted away and external reagents may be sealed out, most decay processes also involve elemental and valence change, such that a compound that is otherwise chemically and physically stable in a particular crystal or amorphous form may be unstable after the decay of a significant portion of one radioactive constituent. Changes in shape, volume or mechanical properties of solid waste forms may then compromise their confinement.

In the present work, we will consider the effects of decay of ^{90}Sr by beta emission into ^{90}Zr (two decays are required, but the intermediate ^{90}Y is short-lived and is not treated here). We employ strontium titanate, SrTiO₃ (abbreviated as STO) as a model host system to understand the effects of replacing divalent Sr by tetravalent Zr. We have performed first-principles computational modeling studies of both the direct replacement of lattice Sr (a Zr_{Sr} impurity) and the addition of interstitial Zr_{int} to the STO lattice. Preliminary experimental results on injection of Zr ions into an STO crystal are also presented. STO is an important technological

material and there is extensive literature [1] on its properties, hence it is a good test material; moreover, ours is the first reported study of Zr addition to STO at low concentrations. We note the publication of a recent computational study [2] of $Sr_{1-x}Zr_xTiO_3$ at higher concentrations ($x = 0.125$, 0.25 and 1) representative of the later stages of SrTiO₃ waste form decay; we will compare our results to theirs in Sections 3 and 5 below.

2. Computational approach

We carried out calculations of minimum-energy atomic geometries, total energies and electronic states using density functional theory (DFT) in the Generalized Gradient Approximation (GGA) as described [3] by Perdew, Burke and Enzerhof (PBE). We thus obtain information only about thermodynamic stability in equilibrium; kinetic effects are left for future studies. Our major focus is to predict the relative abundance of the most common point defects in crystalline Zr-doped STO, and these abundances are determined (for charge-neutral defects) by the grand canonical defect formation energy [4].

$$\Delta H_{defect} = E_{defect} - E_{ideal} - \sum_i \mu_i n_i, \tag{1}$$

where E_{defect} is the total energy of a sufficiently large supercell containing the defect, E_{ideal} is the energy of an ideal supercell containing the same number of primitive unit cells, n_i is the number of atoms of element i added to the ideal cell to produce the defect cell (negative values corresponding to atoms removed) and μ_i is

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the chemical potential for the ith element. The dependence on the chemical potentials reflects the free energy cost of supplying or removing the required number of atoms in an open system, and the concentration of the given defect is then proportional to $\exp(-\Delta H/kT)$ where T is the lowest absolute temperature at which the system was in thermal equilibrium. If E_i is the total energy per atom of an element in its pure bulk form, then we can define a relative chemical potential

$$\mu_i^{\text{rel}} = \mu_i - E_i \tag{2}$$

such that

$$\Delta H_{\text{defect}} = \Delta E_{\text{defect}} - \sum_i \mu_i^{\text{rel}} n_i \tag{3}$$

where

$$\Delta E_{\text{defect}} = E_{\text{defect}} - E_{\text{ideal}} - \sum_i E_i n_i. \tag{4}$$

It is Eq. (4) that is actually computed from electronic structure theory. The full formation energy of Eq. (1) is most easily specified for specific limits of composition; for example when an excess of the ith element is present, such that the bulk element begins to precipitate, the relative chemical potential for that element goes to zero. We consider the effects of the finite unit cell size in our calculations, but do not explicitly treat thermal and vibrational effects. We will, however, discuss volume changes due to defect formation.

The specific implementation of DFT we used for most of our calculations was the periodic linear combination of atomic orbitals (LCAO) code SeqQUEST [5]. This code is computationally very efficient, especially for relatively ionic compounds like STO. We use the Local Moment Counter-Charge (LMCC) method implemented within SeqQUEST for treating charged states of defects without spurious finite-cell Coulomb effects. We employ these capabilities for the charged states of certain non-isovalent defects, for example Zr_{Sr}. Relatively large basis sets and convergence criteria were used, such as to reduce computational errors in total energies to about 0.01 eV/atom. As a test, we repeated several calculations with the projector-augmented-wave DFT code VASP [6], also with high precision settings, and obtained results in excellent agreement with QUEST.

3. Computational results

The formation energy term ΔE from Eq. (4) is shown in Table 1. Energies from VASP are shown in parenthesis. The defect energies vary with cell size but have mostly converged to reasonably stable values at the 135-atom ideal cell dimension ($3 \times 3 \times 3$ supercell of the simple cubic perovskite primitive cell). The metal interstitials

were initially placed at the center of an edge of the primitive cell, with four face-centered oxygen atoms and two corner Sr atoms as nearest neighbors, this being the center of the largest empty space in the ideal lattice. An extended search for a lower minimum energy in the case of the Zr interstitial led to a "dumbbell" geometry, shown in Fig. 1c in which the interstitial atom formed a dimer with a lattice Ti atom; however this geometry only lowered the total energy by 0.10 eV from the more symmetric edge-centered interstitial. The oxygen interstitial was assumed to pair with a lattice O^{2-} ion to form a molecular defect as suggested [7] by other workers. Note that for substitutional Zr_{Sr}, the 40-, 80-, 135- and 160-atom supercells correspond to the composition $Sr_{1-x}Zr_xTiO_3$ with $x = 0.125, 0.0625, 0.03704$ and 0.03125 respectively.

The defect energies reported in Table 1 were obtained with unit cell dimensions held constant at the values derived from the computed bulk structure of STO ($a = 3.949$ Å), which was in close agreement with experiment [8] ($a = 3.905$ Å). However, we also studied the effects of allowing the supercell lattice constants to relax in the presence of a defect, resulting in volume changes and lattice distortions. Results for volume changes are shown in Table 2. As with the total energies, we see that the volume changes per defect are fairly well converged with respect to supercell sizes at the $3 \times 3 \times 3$ supercell.

We observe that the largest volume changes are for interstitials, where the volume increases by up to a few times the mean volume per atom of the bulk (about 12 Å^3). This is consistent with the notion of large compressive stress induced by placing an extra atom into a relatively close-packed structure such as perovskite. Substitutional Zr causes a smaller volume increase on the Ti site, consistent with Zr being slightly larger in atomic radius that the isovalent Ti atom, while Zr on an Sr site causes a small volume contraction, consistent with the large effective atomic radius of the alkaline earths. A strontium vacancy caused a lattice contraction, while the Ti vacancy caused a small expansion due to weakened bonding interactions. The oxygen interstitial causes a smaller volume increase than the metal interstitials because it forms a close molecular dimer with a lattice oxygen ion.

Direct comparison of our defect formation energies with those of Ref. [2] are only possible for the case of one substitutional Zr in a 40-atom cell ($x = 0.125$). The computed energies in Ref. [2] were stated in terms of mean cohesive energies per atom, but we can compare those cohesive energies to our formation energies by subtracting their total cohesive energies from the bulk element cohesive energies computed with VASP [6]. We find that the result of Ref. [2] for $x = 0.125$ corresponds to a value of $\Delta E = 2.67$ eV as defined in our Eq. (4), to be compared with our values of 3.50 or 3.39 eV (40-atom cell, VASP or QUEST method) or 2.66 eV (QUEST, 160-atom cell). The agreement amongst these theoretical results is satisfactory, with the differences in results for the 40-atom cell presumably being due to different choices for convergence parameters, and differences in basis sets and other details of implementation between the three calculations. Reasonable (within about 0.8 eV) agreement was also achieved with the results of Ref. [7] for the formation energies of O and Sr Frenkel defects (vacancy–interstitial pairs).

Charged-cell calculations of defect ionization energies within the LMCC method [5] revealed that the Zr and Ti interstitials are quadruple donors, with all donors levels within the conduction band, so that all excess electrons appear at the conduction band minimum (CBM) with effectively zero ionization energy. Similarly, the Zr_{Sr} substitutional defect is a double donor with both levels in the conduction band. Thus, all the most likely defects associated with conversion of Sr to Zr in STO add excess electrons to band states near the CBM. Since these states have predominantly Ti 3d character, the effect is to slightly reduce the oxidation state of the lattice Ti atoms. For example, with one interstitial Zr added to the 135-atom supercell, four of the 27 lattice Ti atoms would

Table 1
Formation energies ΔE (eV) (Eq. (4)) for various neutral defects, versus number of atoms in the ideal cell. All results are from the QUEST code, except VASP results in parenthesis.

Atoms→	40	80	135	160
V_{Sr}	8.71(8.24)		8.41	
V_{Ti}	14.58(14.62)		14.23	
V_O	5.35(5.27)		4.44	
Sr_{int} (edge)	7.64		6.09	
Sr_{int} (111 dimer)			5.90	
Ti_{int} (edge)	4.52		3.54	
Ti_{int} (111 dimer)			4.22	
Sr_{Ti}	10.13		8.92	
Ti_{Sr}	5.43(5.41)		5.46	
Zr_{Ti}	0.21		0.06	
Zr_{Sr}	3.39(3.50)	3.11(3.23)	3.12(2.98)	2.66
Zr_{int} (edge)	6.68	5.52	5.51	5.05
Zr_{int} (111 dimer)	6.58		5.48	
O_{int} (100 dimer)	1.75		1.41	