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Structural and Electronic Properties of Cr Substituted Ti in Oxygen-Deficient Srtio$_3$: Density Functional Theory Calculations

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Abstract:

Capacitors and gate dielectrics are just two examples of when strontium titanate's dielectric properties would be helpful. The electrical and structural characteristics of Cr-doped B-site $SrTiO_3$ have been investigated using First-Principle simulation. Cr_{Ti} is a shallow acceptor because of the difference in valence between Ti and Cr; the results reveal that substituting a Ti ion Cr ion causes an internal strain originating from the offset between Ti-O and Cr-O bonding lengths. However, oxygen vacancy formation is significantly promoted in oxygen-poor environments. With a binding energy of 0.52±0.09 eV and no states in the gap, we discover that V_o may be attached to Cr_{Ti}. We discussed how Cr_{Ti} could help counteract or capture oxygen vacancy effects.

Keywords: DFT; SrTiO3; Oxygen vacancy; Transition metal; Binding Energy.

1.Introduction

In the past two decades, theoretical and experimental studies have been carried out toward replacing the native oxide in silicon-based devices (SiO_2) with materials with higher relative permittivities, a requirement arising from the shrinking gate thickness uytrdsa1`otherwise resulting in unacceptable tunnelling losses. Numerous binary systems (e.g., Al_2O_3, HfO_2, and TiO_2) have been proposed for this aim. Furthermore, ternary systems represented by dielectrics with the perovskite structure play an important role in maintaining the efficiency of integrated circuits. The high relative permittivity at 300 [1] at room temperature highlights $SrTiO_3$ as a promising alternative dielectric for improving the performance of devices, demonstrated in gate application [2], capacitors, [3] and resistive switching [4–7] applications

The dielectric functionality of thin film $SrTiO_3$ can be optimised by controlling two key parameters: leakage current and dielectric loss. Both theoretical and experimental research into the mechanisms behind resistive switching and the cause of leakage current in $SrTiO_3$ thin film have been published at length [7–11]. Oxygen vacancies (V_o) are typically blamed for the n-type conductivity observed in $SrTiO_3$ thin films. Donor V_o migrates with a barrier of 0.61 to 0.97 eV [12-15], and theoretically, the barrier of the doubly ionised form is 0.72 eV [12-18].

Bi-axial strain as a mechanism for modulating the migration of the oxygen vacancy has been recently presented, joining a number of models that have manipulated the diffusivity and passivated the electrical activity of the vacancy [18, 19]. Doping with non-native elements offers a viable way for compensating or trapping V_o, using acceptor dopants in the B-site influencing n-type conductivity in $SrTiO_3$, [20, 21] other perovskites [22]. This is in addition to the effect of strain on the migration of the oxygen vacancy.

Recent studies exhibiting Cr enhances the photocatalytic performance of $SrTiO_3$[23]. The effects of Cr on the optical and ferroelectric characteristics of SrTiO3 have been demonstrated using a transverse-field Ising mode and the solid-state reaction pathway [24]. This research indicates that Cr occupies the Sr-site due to their ionic radii and charge states. C [25], V [25], Fe [26], Co [27], Mn [28], and Cu [29] are all transition metal impurities that may be hosted at the A-site of $SrTiO_3$, but only to a certain extent. Additionally, it is possible to anticipate local charge compensation by oxygen vacancies following the creation of acceptors in oxygen-deficient $SrTiO_3$ [30].

Despite a growing body of evidence highlighting the role of metallic defects in $SrTiO_3$, the potential impact of Cr, a relatively overlooked element, on the material remains a subject of limited exploration. Of particular interest is the possibility of Cr serving as a capturing site for electrically active oxygen vacancies in $SrTiO_3$. This study aims to systematically investigate the structural, electrical, and optical properties associated with Cr in $SrTiO_3$, with a focus on altering these properties through computational material design. First-principles simulations offer a reliable avenue for guiding experimental investigations.

In this work, we employ density functional theory calculations to examine the binding of oxygen vacancies to Cr-doped B-site in $SrTiO_3$, along with exploring various structural and electronic characteristics of the material.

2. Computational Method And Models

Spin-polarised local density functional [33] computations were performed in the Ab-Initio Modeling Program code [31, 32] to study the structural and electronic characteristics of Cd-doped SrTiO3. The structural and electronic features of the oxygen vacancy in conjunction with the Cr-doped Ti-site have been studied.

The electron-ion interactions were simulated employing a norm-conserving Pseudopotential [34]. The valence configurations utilized for Sr, Ti, Cr, and O were 4s24p65s2, 3s23p63d24s2, 3s2 3p6 3d4 4s2, and 2s22p4, respectively. Titanium, Chromium, and oxygen were described using four sets of s-, p-, and d-Gaussian functions, resulting in a total of 40 functions per atom. These functions were employed to represent electronic wave functions using atom-centered Gaussian basis functions [35]. The Hamiltonian matrix elements were determined through a plane-wave expansion of density and Kohn-Sham potential [36], with a cutoff energy set at 300 Ha.

The computational method employed in our study yields an equilibrium lattice parameter of 3.88 ˚A for bulk SrTiO3, which is consistent with prior results [37] and experiment [41]. A similar computational approach has been successfully adopted to explore the oxygen vacancy migration under bi-axial tensile,[19] compressive strain, [18] as well as the electronic structure of the hydrated SrTiO3 (001) surface [39].

The structural optimization process utilizes the conjugate gradients method to achieve optimized structures, ensuring that forces acting on each atom remain below 10-3 atomic unit. In the final phase, a reduction in total energy to below 10-5 Ha is sought to establish equilibrium structures. Allowing all atoms to move freely is crucial in determining these equilibrium configurations. Moreover, symmetry constraint conditions are avoided during optimization by comparing the energy of each defect structure to the lattice symmetry.

The Binding Energy of the complex CrTi-Vo is defined as the discrepancy in total energies between the individual components and the complex.

$$E^b(Cr_{Ti}, V_o) = E^T(Cr_{Ti}) + E^T(V_o) - E^T(Cr_{Ti}, V_o) - E^T{}_{pure} \quad (1)$$

Where the total energies of Vo and CrTi in their isolated forms are ET (Vo) and ET (CrTi), respectively. The total energy of the complex is ET (CrTi, Vo) and Epure for pure strained SrTiO3. In the calculation of CrTi–Vo binding energies, different cell sizes have been adopted. The table shows the lattice type, vectors, and number of atoms. Unless stated otherwise, the results are based on 135 atom cell calculations.

Table 1.Describes the super-cells employed in the present study. An is the primitive unit cell's lattice constant in SrTiO3.

No. atoms	Lattice	Vectors
80	Face-centered cubic	$\sqrt{2}[aa0] \times 2\sqrt{2}[a0a] \times 2\sqrt{2}[0aa]$
135	Simple cubic	$3[a00] \times 3[0a0] \times 3[00a]$

3. Results and Discussion

The optimised structure with Cr instead of Ti is displayed in Figure 1. To begin, we will go over the optimised geometry. Referring the bonding in rock-salt CrO. The six neighbouring oxygen ions of CrTi (labelled (a) in Fig.1) are similar. Furthermore, it is observed that the distance between oxygen ions and Cr is 3.78 ˚A in the studied system, which is less than the 4.22 ˚A calculated lattice constant for the rock-salt phase of CrO. This measured separation differs from values reported in experimental studies 4.28 ˚A [40, 41] and theoretical calculations 4.24 ˚A [42] and 4.23 ˚A [40].

The inclusion of CrTi is found to cause the lattice to tense due to the Cr-O bond lengths being shorter than host Ti-O bonds. The small ionic radius of Cr+2 (0.615˚A) compared to Ti+4 (0.68˚A) is another possible explanation for the tension.

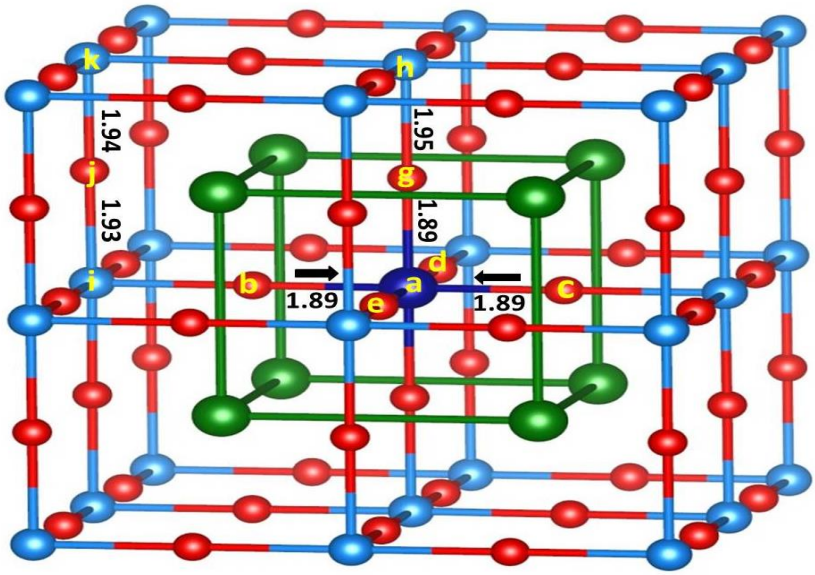

Fig. 1. The optimised Cr_{Ti} core in SrTiO3 is structured schematically. The green, grey, red, and blue spheres symbolise Sr, Ti, O, and Cr. The six oxygen ions following the Cr ions are labelled b-g, and the little arrows show the direction of travel during optimization. Selected bond lengths are shown in ˚A. The system is set up so that the vertical and horizontal directions are [001] and [100], respectively, with an off-axis presentation to improve understanding.

Figure.1 shows the Ti-O bond lengths, which indicates that the tension surrounding the Cr site is somewhat limited. In contrast to bulk SrTiO3, which has a bond length of 1.89 ˚A, the bond between atoms i and j is slightly lengthy, measuring 1.93 ˚A. The Ti-O bond that is parallel to the Cr-O bond (g to h) is only 1.95˚A, which is approximately 5% less than the bulk version of the same bond.

As previously indicated, CrTi causes a local dilatation of the lattice. Cr can relax towards the vacancy in the complex (Fig.3), making it easier to accommodate the Cr ion. Specifically, the 1.79 ˚A and 1.77 ˚A axial Cr-O and Ti-O bond lengths, respectively, show that the relaxation of the ions linked to the vacancy is different.

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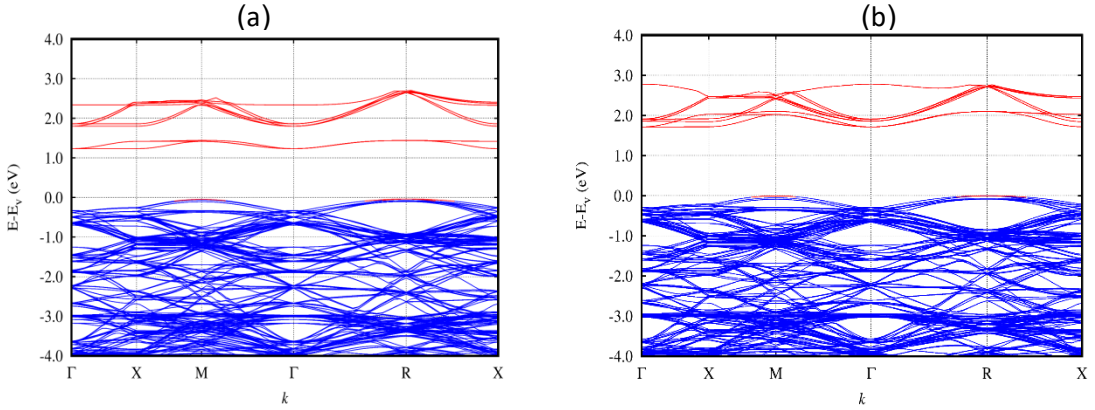

Fig. 2. The electronic band structure near the band gap for (a) neutral Cr_{Ti} and (b) Cr_{Ti} in the -2 charge state in $SrTiO_3$, along high symmetry directions in the Brillouin zone with the valence band top as the reference energy level set to zero.

Furthermore, it is anticipated that this complex will be formed as a result of the electrostatic interactions. Since VO is a double donor, as is well-established in the literature, the combination can be characterised as CrTi2--VO+2. It is believed that this pair of acceptors and donors will form an isoelectronic defect and will be bound Coulombically.

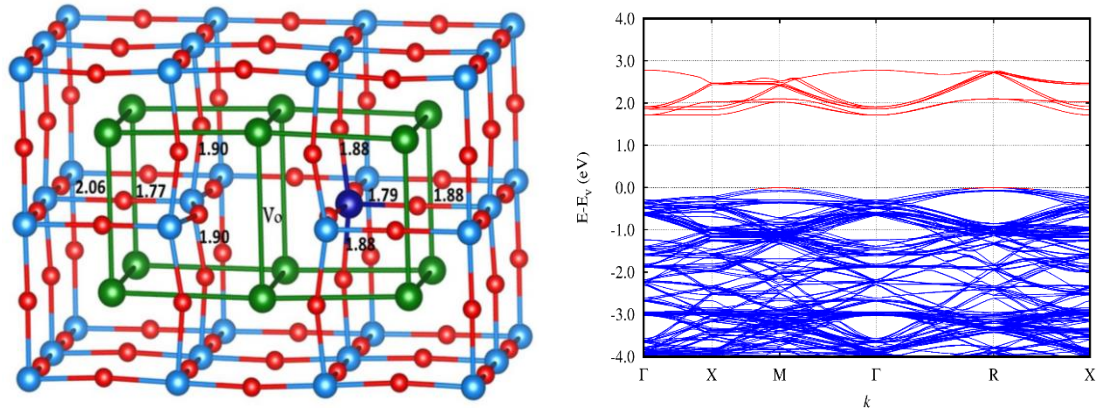

Fig. 3. Diagram illustrating the optimised structure of Cr_{Ti}-Vo (on the left), with colours and labels matching those in Figure 1. The electronic band structure (on the right) shows high symmetry directions in the Brillouin zone near the band gap for Cr_{Ti}-Vo.

Systems composed of CrTi and Vo have, therefore, been modelled. The vacancy has the probability to be located in the first, second, and third oxygen shells with respect to the Cr site, progressively farther away from CrTi. All these sites of the vacancy has been investigated to find the energetically favorable site. We observe that Vo has an energy preference for the first adjacent oxygen shell, which means it misses one of the six oxygen ions linked to the Cr ion (sites b-g in Fig.1). As illustrated in Figure.3, this nearest-neighbour pair has an optimised structure. Figure.2(b) shows that the defect complex does not generate any band-gap states. Both structural and electrical aspects contribute to the Vo propensity to develop in close proximity to Cr ions.

The binding energy magnitude of the reaction

$$Cr_{Ti} - V_o =\leftrightarrow Cr_{Ti}^{-2} + V_0^{+2} \quad (2)$$

Computed using formula 1. We estimate a binding energy of around 0.52±0.09 eV based on the three largest cell sizes. For all cell sizes except the smallest one, the computed binding energy falls within a reasonably narrow range of values. At ambient temperature, this number suggests that the two faults are associated. Not only that, but the computed binding energy is greater than the values published for AlTi-VO (0.15 eV) [47] and FeTi-VO (0.3-0.4 eV) [46].

Assuming the dissociation barrier is equal to the sum of the binding energy and the migration barrier of VO+2 (calculated at 0.72 eV) [18], we arrive at a temperature of approximately 600 K for a process that follows Boltzmann statistics, with a dissociation rate of 1 Hz and an attempt frequency of 16 THz. So, this may be seen as a ballpark figure for the growth temperature at which CrTi and an adjacent oxygen vacancy are likely to be integrated and the temperature at which annealing the material is required to activate the CrTi acceptors. Given the comparatively high binding observed in the case of CrTi inclusion as isolated acceptors, CrTi can be considered as a potential room temperature trap for Vo in SrTiO3.

The CrTi-Vo electronic structure is illustrated in Figure.3. It is possible that the band gap may somewhat rise at the simulation concentration of Cr substitution of Ti of about 3%. When Ti is substituted with Cr in BaTiO3, a similar pattern of behaviour is seen [44]. Moreover, the electron chemical potential is found to be just below the valence-band top in the calculations, which raises the possibility of p-type conductivity for SrTiO3 that is related to Cr. Because of this electron deficiency, the electrons that are produced during Vo production may be trapped.

If CrTi is a double acceptor and, depending on the position of level, leads to p-type conductivity, it would make sense because Ti and Cr are expected to have different formal oxidation states at this site. Since Vo generation is typically associated with as-grown n-type conductivity, an acceptor could be a way to remove the electrons produced from Vo. There has been prior research on this compensating mechanism in studies analysing the reduction conditions in SrTiO3 with 3d-transition metal doping [43]. Finding out what CrTi electrical and electronic characteristics are is thus of particular importance.

4. Conclusions

Through the application of density functional theory, we conducted a study on the impact of replacing Ti with Cr in SrTiO3 on its electrical and electronic properties. Our findings indicate that CrTi induces slight local structural changes around the defect, creating a shallow acceptor level, potentially leading to the formation of P-type SrTiO3. The interaction between CrTi double acceptors and the prevalent oxygen vacancy double donors is energetically favorable. Specifically, oxygen vacancies tend to favor the vicinity of the first oxygen shell and then localise near the Cr ion.

The resultant defect, electrically inert in nature, can be considered a pair of double acceptors and double donors, or in terms of crystal composition, as a local alloy comprising SrTiO3, SrO, and CrO. For instance, in simulations using a 135-atom supercell, the defect-free system can be described as (SrTiO3)32, while the defective system is represented as (SrTiO3)31(SrO)(CrO). This implies that a stoichiometric CrO unit substitutes a native stoichiometric TiO2 group. This system shows promise as a candidate for capturing oxygen vacancies due to its positive binding energy (0.52±0.09 eV), which is relatively high compared to previously studied Fe and Al substitutions. The binding of the CrTi-Vo complex is expected to hold up to approximately 600K.

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