First-Principles Study of Intrinsic Defects on Bulk SrTiO₃†

XIAOQIU WANG[1], BAOLING WANG[2] and QINFANG ZHANG[2,3,*]

[1]Department of Physics, Jinling Institute of Technology, Nanjing 211169, Jiangsu Province, P.R. China
[2]Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province, Yancheng Institute of Technology, Yancheng 224051, P.R. China
[3]Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, P.R. China

*Corresponding author: Fax: +86 515 88298920; E-mail: qfangzhang@ycit.edu.cn

Intrinsic defects on bulk $SrTiO_3$ using first-principles calculations based on the density functional theory were studied. It has been shown that the relative stability of defect samples is strongly dependent on the atomic chemical potentials. The Ti (Sr) vacancy is more stable in bulk $SrTiO_3$ under high oxygen partial pressure (PO_2). In contrast the O vacancy is energetically favorable under the reduction condition. Furthermore, it is found that the defect system with Sr vacancy is non-magnetic metal, while Ti vacancy may induce ferromagnetism in bulk $SrTiO_3$.

Keywords: First principles, Defects, Magnetism.

INTRODUCTION

Intrinsic defects, *e.g.* cation or anion vacancies, in complex oxide materials are believed to be responsible for various exotic electronic quantum properties and may also be important for many engineering applications. An ideal example is netural defects in $SrTiO_3$. Single crystal $SrTiO_3$ has long been used as the substrate of choice for the epitaxial growth of various kinds of complex oxides, due to its compatible lattice parameters, structure, commercial availability, controllable surface termi-nation, tailorable conductivity and comparatively low chemical reactivity[1-3]. $SrTiO_3$ is a model compound belonging to the perovskite family which crystallizes in the cubic Pm3m space group at room temperature with a lattice parameter of 3.905 Å(Fig. 1), undergoing a symmetry-lowering transition to a tetragonal structure below 105 K. The electrical conductivity and optical studies reveal that $SrTiO_3$ is commonly an insulator with a band gap of 3.2 eV at room temperature[4]. By substituting only a small amount of Sr with La or Ti with Nb or Ta, the material can become highly conducting (n-type) with carrier concentration as high as 10^{-19} cm^{-3}[5]. Similarly, it can also become a p-type conductor by substituting small amount of Ti with trivalent metals like In, Al, Fe and Sc[6]. It even exhibits super-conductivity with transition temperature of around 0.3 K and it has been pointed out that this transition in $SrTiO_{3-\delta}$ can be

induced by O vacancies as low as 0.03 percent[7]. Furthermore, it is also inherently a quantum paraelectric and with the aid of an external mechanical stress, such as from epitaxial strain of a thin film, a stable ferroelectric phase can be achieved[8]. Recent studies also suggest that two-dimensional electron liquid state of $LaAlO_3/SrTiO_3$ heterostructures is driven by the oxygen vacacies in the $SrTiO_3$ layer generated by the deposition of the $LaAlO_3$ film[9].

Despite of many of the above-mentioned fascinating properties, roles of the intrinsic defects in $SrTiO_3$ are still far from understood. To study the intrinsic defects and the electronic band structure of such as complex oxides, Rusydi *et al.*[10] have recently developed a new experimental method, a combined ultraviolt-vacuum ultraviolet (UV-VUV) reflectivity and spectrocopic ellipsometry setup covering photon energy range from 0.5 to 35 eV. They show the importance of the high energy optical conductivity in order to reveal the intrinsic defects and the complex nature of electronic band structure of $SrTiO_3$. Herewith, we have studied on the intrinsic defects in bulk $SrTiO_3$ using the first-principles density funcitonal theory. We find that the relative stability of the defect samples is strongly dependent on the atomic chemical potentials. Ti (Sr) vacancy can be stable on high oxygen partial pressure, while the O vacancy is energetically favorable under low oxygen partial pressure.
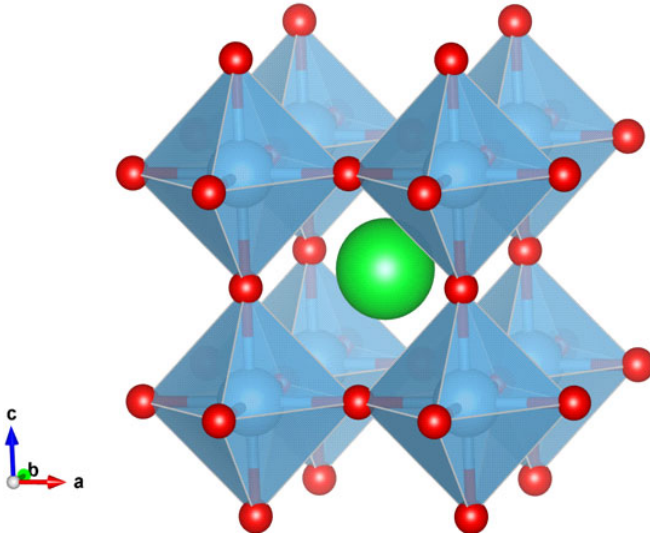
Fig. 1.   Systematic figure of crystal structure of SrTiO$_3$. Here octahedral cages surrounding Ti are denoted by blue, O by small red spheres and Sr is denoted by large green spheres

METHODOLOGIES

In this study, first principles plane-wave based calculations with the generalized gradient approximation (GGA) were performed using *VASP* code. We also consider the on-site coulomb interaction of *d* orbitals of titanium and the effective Hubbard U is taken as 4.36 eV. We use 3 × 3 × 2 supercell to simulate defect effect on cubic perovskite structure of SrTiO$_3$. For a single O (Sr or Ti) vacancy, one oxygen (Sr or Ti) atom is removed out of supercell. All the atoms in these defective supercells were full relaxed until the atomic forces were below 0.01 eV/Å.

The formation energies of vacancies in SrTiO$_3$ were calculated from total energies of the supercells, based on the standard formalism by Zhang and Northrup[11]. For a vacancy with a charge state q, the formation energy is given by

$$E_f = E_T(defect{:}q) - \{E_T(perfect) - n_{Sr}\mu_{Sr} - n_{Ti}\mu_{Ti} - n_O\mu_O\} + q(\varepsilon_F + E_{VBM}) \quad (1)$$

Here $E_T(defect{:}q)$ is the total energy of the supercell containing a vacancy with a charge state q; n_{Sr}, n_{Ti} and n_O are the number of Sr, Ti and O atomic vacancies; μ_{Sr}, μ_{Ti} and μ_O are the atomic chemical potential; and ε_F is the Fermi energy measured from the valence band maximum (VBM). It is known that the formation energies of vacancies in SrTiO$_3$ depend on atomic chemical potentials μ_{Sr}, μ_{Ti} and μ_O. In case of the ternary SrTiO$_3$ system, the atomic chemical potentials are determined from equilibrium conditions of various phases containing Sr, Ti and O atoms. In general it is assumed that bulk SrTiO$_3$ is stable and the chemical potential of three elements have to satisfy the following condition:

$$\mu_{Sr} + \mu_{Ti} + 3\mu_O = \mu_{SrTiO_3(bulk)} \quad (2)$$

$\mu_{SrTiO_3(bulk)}$ is the chemical potential of bulk SrTiO$_3$. In this work we considered the oxidation (Case A and B) and the reduction (Case C, Case D and Case E) conditions on the same foot.

In case A, SrTiO$_3$ is in the equilibrium with O and SrO, then

$$\mu_{Sr} + \mu_O = \mu_{SrO(bulk)}, \text{ and } \mu_O = \mu_{O(bulk)} \quad (3)$$

In case B, SrTiO$_3$ is in the equilibrium with O and TiO$_2$, then

$$\mu_{Ti} + 2\mu_O = \mu_{TiO_2(bulk)}, \text{ and } \mu_O = \mu_{O(bulk)} \quad (4)$$

In case C, SrTiO$_3$ is in the equilibrium with Ti and TiO, then

$$\mu_{Ti} + \mu_O = \mu_{TiO(bulk)}, \text{ and } \mu_{Ti} = \mu_{Ti(bulk)} \quad (5)$$

In case D, SrTiO$_3$ is in the equilibrium with Sr and SrO, then

$$\mu_{Sr} + \mu_O = \mu_{SrO(bulk)}, \text{ and } \mu_{Sr} = \mu_{Sr(bulk)} \quad (6)$$

In case E, SrTiO$_3$ is in the equilibrium with Sr and Ti, then

$$\mu_{Ti} = \mu_{Ti(bulk)}, \text{ and } \mu_{Sr} = \mu_{Sr(bulk)} \quad (7)$$

In order to determine the atomic chemical potentials, we also calculated total energies of the bulk systems of Sr(fcc), Ti(hcp), SrO(Fm3m), TiO$_2$(P42/mmm) and TiO(Fm3m) at their equilibrium states. The oxygen chemical potential μ_O is obtained from the total energy of O$_2$ molecule using a cubic supercell 15 × 15 × 15 Å^3.

RESULTS AND DISCUSSION

Using the density functional theory calculations we obtain that the optimized lattice constant of bulk SrTiO$_3$ is 3.943 Å, which agrees well with the experimental data (3.905 Å). As we know that the GGA calculations always underestimate the band gap of the material and the band gap of SrTiO$_3$ is only 1.77 eV based on our GGA calculation, which is almost half of experimental value. Even with GGA + U technique, it increases only up to 2.35 eV, being still significantly smaller than experimental one.

We adopt the GGA+U method to deal with all defective supercell calculations below. In this work we considered charge neutral defect samples, which are Sr vacancy (V$_{Sr}^0$), O Vacancy (V$_O^0$), Ti Vacancy (V$_{Ti}^0$), Sr partial schottky reaction (V$_{Sr}^{2-}$ + V$_O^{2+}$), Ti partial schottky reaction (V$_{Ti}^{4-}$ + 2V$_O^{2+}$) and full schottky reaction (V$_{Sr}^{2-}$ + V$_{Ti}^{4-}$ + 3V$_O^{2+}$). The formation energies of various defect samples are compared in Fig. 2. We found that at high oxygen partial pressure Sr (Ti) vacancy is more stable, but O vacancy will be energetically favorable in reduction condition. In case A, SrTiO$_3$ is in the equilibrium with O and SrO and Sr vacancy is easy to appear in bulk SrTiO$_3$. In case B, SrTiO$_3$ is in the equilibrium with O and TiO$_2$, Ti vacancy is energetically more favorable than other netural defects. In case C, D and E, the reduction condition is of advantage to oxygen vacancy.

The oxygen vacancy has been well studied in bulk SrTiO$_3$; for instance, it has been found[12] that it can induce a local antiferrodistortive-like oxygen-octahedron rotation, even in the cubic phase. This feature leads to in-gap localized electronic states, giving a convincing explanation for the thermal ionization and optical transition that are observed experimentally. The oxygen-octahedron rotation around the oxygen vacancy thus plays a key role in the physical properties of SrTiO$_3$. Here we focus on the Sr and Ti vacancies occurred on SrTiO$_3$ under the oxidation condition. It's much interested to study the electronic and magnetic properties of defect SrTiO$_3$ systems. In order to investigate the magnetic exchange interaction of the defects states, we double the supercell of SrTiO$_3$ and consider both ferromagnetic and antiferromagnetic interaction
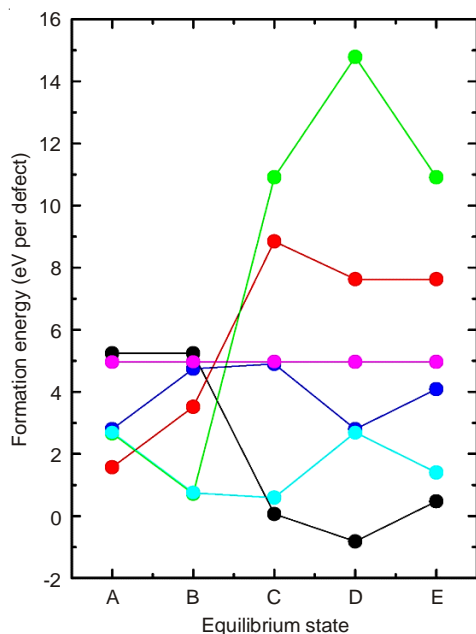
Fig. 2. Defect formation energies of isolated neutral vacancies in $SrTiO_3$ at various equilibrium states: (red-circles) charge neutral defect with Sr vacancies (V_{Sr}^0), (black-circles) O vacancies (V_O^0), (green-circles) Ti vacancies (V_{Ti}^0), (blue-circles) Sr partial Schottky reaction ($V_{Sr}^{2-} + V_O^{2+}$), (cyan-circles) Ti partial Schottky reaction ($V_{Ti}^{4-} + 2V_O^{2+}$) and (magenta circles) full Schottky reaction ($V_{Sr}^{2-} + V_{Ti}^{4-} + 3V_O^{2+}$)

between the defects. It was found that spin polarized state is most stable for Ti vacancy system (Table-1), but for $SrTiO_3$ with Sr vacancy the ground state is always nonmagnetic. Furthermore, in Ti-defect system the ground state is ferromagnetic (FM), which has lower energy compared to the anti-ferromagnetic (AFM) and non-magnetic (NM) states.

TABLE-1
ENERGIES OF MAGNETIC STATES RELATED TO
NONMAGNETIC STATE IN TI VACANCY

NM (meV)	FM (meV)	AFM (meV)
0	-29.6	-10.0

The density of states for bulk $SrTiO_3$ with Ti vacancy or Sr vacancy are shown in Fig. 3. From Fig. 3(a) and (c) it is clear that both systems are metallic. To further investigate the origin of the magnetic properties in Ti defect system, the partial density of state of oxygen is also shown in Fig. 3(b). We found that magnetism in Ti defect system is due to the spin-polarized oxygen atoms, which are located as nearest neighbor of Ti vacancy. This unusual defect mediated magnetism, not based on *d* or *f* electrons, displays a new way to utilize the magnetic materials.

Conclusion

Using the density functional theory, we have studied the defects stabilities of bulk $SrTiO_3$ as the function of atomic chemical potential. We find that the relative stability of the defect samples is strongly dependent on the atomic chemical potentials. Ti (Sr) vacancy can be stable on high oxygen partial pressure, while the O vacancy is energetically favorable under low oxygen partial pressure. These different types of defects may mediate with magnetic and electronic properties of bulk $SrTiO_3$. For instance, the defect system with Ti vacancy is
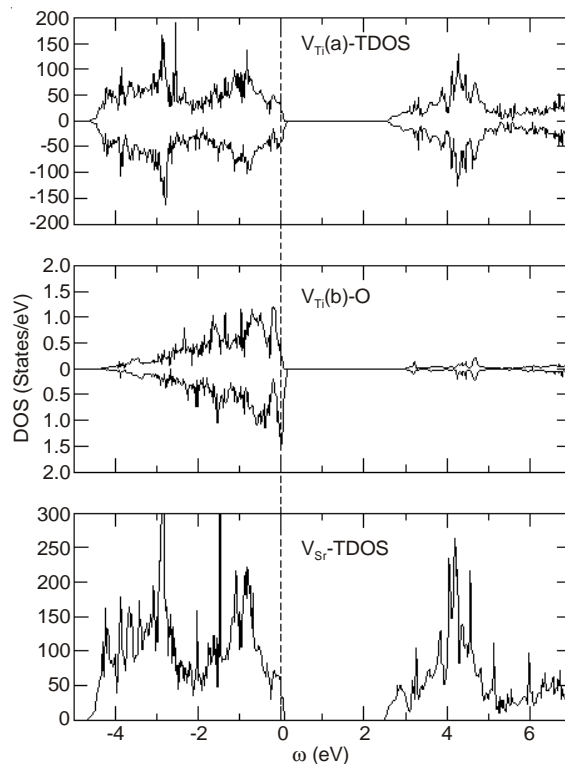

Fig. 3. Density of states for Ti vacancy and Sr vacancy

ferromagnetic metal, while the defect one with Sr vacancy is nonmagnetic metal.

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