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# First-principles study of CaTiO<sub>3</sub> oxygen-vacancies (0 0 1) surface

Hanying Wang<sup>a,\*</sup>, Guozhang Wang<sup>a</sup>, Xiumei Wei<sup>b</sup>, Jie Cui<sup>c</sup>

<sup>a</sup> Energy Engineering Department, Yulin University, Yulin 719000, Shaanxi, PR China

<sup>b</sup> College of Physics and Information Technology, Shannxi Normal University, Xi'an 710062, Shaanxi, PR China

<sup>c</sup> School of Materials Science and Engineering, Xi'an University of Technology, Xi'an 710048, Shaanxi, PR China

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## ABSTRACT

The structural and electronic properties of fully relaxed CaTiO<sub>3</sub> oxygen-vacancies (0 0 1) surface with CaO and TiO<sub>2</sub> terminations are investigated by first-principles plane waves ultrasoft pseudopotential method based on local density approximation. The present results show that the direction and the magnitudes of the atomic relaxations for oxygen-vacancies surface are different from that of the perfect surface. Compared with the TiO<sub>2</sub>-terminated oxygen-vacancy surface, the CaO-terminated oxygen-vacancy surface are likely to be observed in oxygen environment conditions. Much different from the perfect surface, the oxygen-vacancy surface becomes metallic caused by some states in the conduction band are lowered and pulled down in the band-gap region.

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## 1. Introduction

ATiO<sub>3</sub> perovskite ferroelectric films are important for many high-tech applications, including high-capacity memory cells, catalysis, optical waveguides, integrated optics applications [1–3]. With the increasing requirement of multifunctional, integrational and micromaterial to electronic appliance by informational times, the perovskite ferroelectric films of low-dimension and minisize have become the highlights of current researches.

Cubic CaTiO<sub>3</sub> is widely used in electronic ceramic materials. Particularly, being a key component of Synroc, it is used to immobilize nuclear waste [4]. The critical transition temperature for CaTiO<sub>3</sub> from the cubic to low temperature phase is 1580 K. Recently, the influence of three low index perfect surfaces effect on their structural and electronic properties has been studied extensively in theoretics [5–8]. Wang et al. have examined the (0 0 1) surface and found that the TiO<sub>2</sub>-terminated (1 0 0) surface is energetically preferred over the BaO- and SrO-terminated (1 0 0) surface for BaTiO<sub>3</sub> and SrTiO<sub>3</sub>, however, the CaO-terminated (1 0 0) surface is preferred to the TiO<sub>2</sub>-terminated (1 0 0) surface for CaTiO<sub>3</sub> since the Ca<sup>2+</sup> is the smallest +2 cation in these titanates [5]. The study on the (1 1 0) surface calculated by Zhang et al. shows that the Ca termination is stable in O- and Ca-rich environments, and its complementary TiO termination is stable in O- and Ca-poor conditions [6].

It is known that point defects on perovskite surfaces play an important role through control of optical, catalytic and transport [9,10]. Especially, the oxygen-vacancies on the surface of thin solid films are usually inevitably appeared by annealing. However, to our knowledge, the influences of oxygen-vacancies for the CaTiO<sub>3</sub> surface have not been investigated until now. In the present work, we restrict ourselves to the cubic phase and focus on the properties of (0 0 1) oxygen-vacancy surface. The atomic structures and electronic properties of the fully relativistic slab layer of the CaTiO<sub>3</sub> (0 0 1) oxygen-vacancy surfaces with TiO<sub>2</sub>- and CaO-terminated have been systematically investigated.

## 2. Method

All calculations were performed within the framework of density functional theory implemented in the CASTEP (Cambridge Serial Total Energy Package) [11]. The electron-ion interactions were described by ultrasoft pseudopotentials and electron exchange and correlation energies were calculated with the CA-PZ formulation of the local density approximation (LDA) [12]. The structure was optimized with the BFGS method [13]. The pseudopotentials used for bulk and slabs were constructed by the electron configurations as Ca 3s<sup>2</sup>3p<sup>6</sup>4s<sup>2</sup> states, Ti 3s<sup>2</sup>3p<sup>6</sup>3d<sup>2</sup>4s<sup>2</sup> states, and O 2s<sup>2</sup>2p<sup>4</sup> states. The kinetic energy cutoff (400 eV) of the plane wave basis was used throughout and the Brillouin zone was sampled with special k-points of an 8 × 8 × 8 grid for cubic structure, a 6 × 6 × 1 grid for TiO<sub>2</sub>-terminated oxygen-vacancy surface and a 6 × 3 × 1 grid for CaO-terminated oxygen-vacancy surface, as proposed by Monkhorst and Pack [14]. The convergence

\* Corresponding author.

E-mail address: hanyingwang@yahoo.cn (H. Wang).

with respect to the cutoff energy and the k-points mesh has been tested and the results show that the cutoff energy and the k-points mesh used in this work are enough for the system. The energy tolerance was  $5.0 \times 10^{-6}$  eV/atom, the force tolerance was 0.01 eV/Å, and the displacement tolerance was  $5.0 \times 10^{-4}$  Å.

Before the surface calculations, the bulk lattice constant  $a$  is calculated firstly and the result of 3.808 Å is slightly smaller than the experimental value of 3.895 Å [15], confirming the suitability of the local density approximation in this compound. The theoretical lattice constant is used in following surface calculations.

The cubic  $\text{CaTiO}_3$  (001) perfect surface consists of two types of neutral termination, with the sequence of atomic layers of CaO and  $\text{TiO}_2$  (displayed in Fig. 1(a)). In this paper, we consider two types of (001) terminations and the neutral oxygen-vacancy, simply by setting the charge of oxygen-vacancy to zero, is introduced as the defect in the two termination surfaces (shown in Fig. 1(b) and (c)). A periodic slab of nine layers with CaO and  $\text{TiO}_2$  stacked alternately is used to model the surface, separated by a 12 Å vacuum region. During the surface structure optimization, all atoms are fully relaxed.

### 3. Result and discussions

#### 3.1. The surface relaxation

The relaxed structures of  $\text{CaTiO}_3$  perfect and oxygen-vacancies (001) surface with CaO and  $\text{TiO}_2$  terminations have been calculated, and the results are listed in Table 1. The displacements of the atom on  $i$ th layer from the surface are expressed as  $\Delta z_i$ :

$$\Delta z_i = (z_i - z_{i,bulk})/a \times 100\%, \quad (1)$$

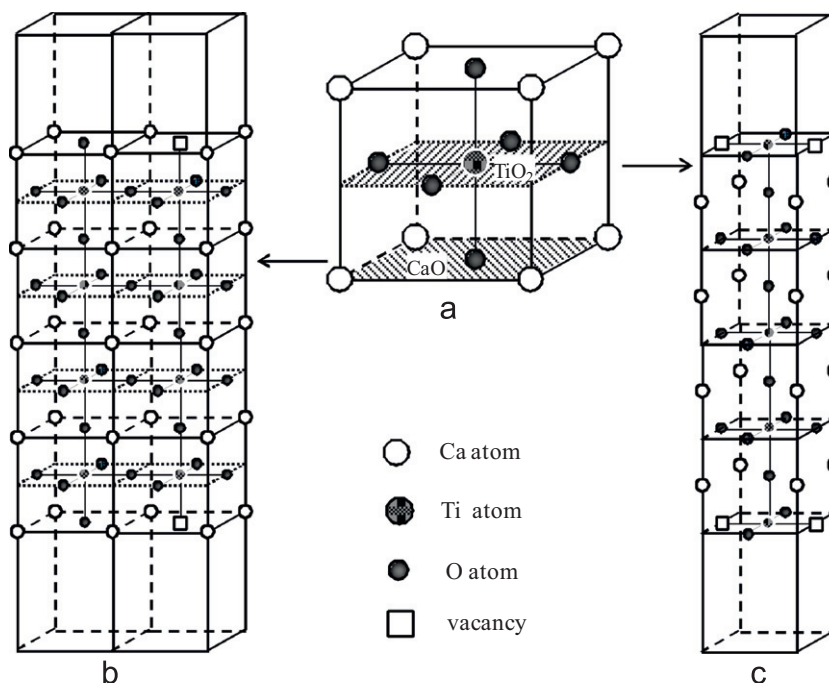
Here,  $z_i$  is the  $z$  coordinate of Ca, Ti and/or O in the  $i$ th layer after relaxation,  $z_{i,bulk}$  is the unrelaxed  $z$  coordinate determined from the theoretical lattice constant. Negative values of  $\Delta z_i$  denote the direction inwards the surface, on the contrary, positive values of  $\Delta z_i$  are related to the direction outwards the surface.

From Table 1, we can see that the relaxation results of the perfect surface are in agreement of the previous calculations [16,7]. The largest relaxations are on the surface layer atoms for the CaO-termination, whereas the largest relaxations are on the subsurface layer atoms for the  $\text{TiO}_2$  termination. For the oxygen-vacancy surface, the direction and the magnitudes of the atomic relaxations are different from that of the perfect surface. First of all, the displacements of O atoms in the oxygen-vacancy surface are larger than that of in the perfect surface. For the CaO termination oxygen-vacancy surfaces, the largest relaxations of Ca atoms in the first layer move inward by 7.99%, whereas O atoms move outward by 0.98%. For the  $\text{TiO}_2$  termination oxygen-vacancy surfaces, the largest relaxations are also on the subsurface layer atoms (Ca atoms for  $-3\%$ ), but the directions of the atomic relaxations are different from that of the perfect surface. For the perfect  $\text{TiO}_2$  termination, Ti and O atoms in the first layer both move inward. However, for the oxygen-vacancy surface, the

**Table 1**

The atomic displacements of two terminations with respect to ideal positions in percent of bulk lattice constant for the perfect and oxygen-vacancy surface.

Termination	Layer	Atom	Perfect surface			Oxygen-vacancy surface Present work
			Present work	GGA [16]	B3PW3 [7]	
CaO	1	Ca	-8.87	-8.8	-10.7	-7.99
		O	0.74	0.7	-0.73	0.98
	2	Ti	1.97	2.7	1.04	0.98
		O	0.21	1.2	-0.74	4.41
	3	Ca	-2.23	-3.2	-2.93	-5.80
		O	-0.03	-0.1		0.41
$\text{TiO}_2$	1	Ti	-2.8	-2.9	-3.72	-1.44
		O	-1.18	-0.5	-2.03	2.77
	2	Ca	5.38	7.7	5.48	-3.00
		O	0.26	0.8	0.21	1.55
	3	Ti	-0.63	-0.9	-1.03	-0.38
		O	-0.26	-0.9	-0.72	1.23



**Fig. 1.** Schematic illustrations of the models: (a) two terminations of the perfect (001) surface; (b)  $2 \times 1$  cell for oxygen-vacancy surface with CaO termination; (c)  $1 \times 1$  cell for oxygen-vacancy surface with  $\text{TiO}_2$  termination.

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