First principles studies on the structural and electronic properties of $Sr_{n+1}Ti_nO_{3n+1}$ ($n=1, 2, 3, \infty$)

Y.C. Zuo [a], C.Y. Ouyang [a,b,*], S.Q. Shi [b], M.S. Lei [a]

[a] *Department of Physics, Jiangxi Normal University, Nanchang 330022, China*
[b] *Renewable Energy Laboratory, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*

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ABSTRACT

Structural and electronic properties of $Sr_{n+1}Ti_nO_{3n+1}$ ($n=1, 2, 3, \infty$) are studied using first principles calculations. Differences in these properties of $Sr_{n+1}Ti_nO_{3n+1}$ are compared. There are two kinds of O in $Sr_{n+1}Ti_nO_{3n+1}$ from the structural point of view: one coordinated and two coordinated O. From analysis on the density of states projected to different atoms, the bonding nature is discussed. Although Ti–O bonds are mainly ionic when O atom is bonded with two Ti atoms, a certain covalent feature is clearly observed. When the O atom is bonded with only one Ti atom, the Ti–O bond is completely ionic. We also verified the interaction between Ti and O by analyzing the band decomposed charge densities.

1. Introduction

The cathodes in solid oxide fuel cells (SOFC) need to meet the requirement of high electronic conductivity under oxidizing atmospheres, which is quite different from that experienced in the anode chamber. Doping can alter the structural stability, catalytic activity, and ionic and electrical conductivities of the perovskite [1,2]. Either through transition-metal redox processes or by doping to the perovskite A or B sites with lower valence cations, oxygen vacancies are introduced into the lattice. The oxides with the perovskite structure can be tailored considerably to achieve certain desired properties [3–5]. By cutting the cubic perovskite $SrTiO_3$ along the [1 0 0] direction and then followed by an insertion of additional oxygen, the perovskite structure can be tailed into a series of structures $Sr_{n+1}Ti_nO_{3n+1}$ ($n=1, 2, 3...$), which are called the Ruddlesden–Popper (RP) phases [6].

The electronic structure of $SrTiO_3$ has been studied extensively in the literature [7–11]. These studies suggest that the top of the valence band is made up predominately of the oxygen 2p states and the bottom of the conduction band has a Ti-3d character. Due to the interaction between Ti-3d and O-2p, it is found that the network of corner-shared TiO_6 octahedral dominates the main electronic properties of $SrTiO_3$ [12]. Although there are a lot of similarities among the structures of $Sr_{n+1}Ti_nO_{3n+1}$ ($n=1, 2, 3, \infty$)

in view of the TiO_6 octahedral, they show a lot of differences in their physical properties. The band gap of Sr_2TiO_4 is enlarged compared to that of $SrTiO_3$ [13–15]. Furthermore, owing to the randomly distributed insulating Sr–O layers in polycrystalline RP phases, their lower thermal conductivity compared to $SrTiO_3$ makes Sr_2TiO_4 and $Sr_3Ti_2O_7$ attractive for thermoelectric applications if their electronic properties can be improved. It was found that large TE power can be obtained in conjunction with high symmetry TiO_6 octahedral [16].

While there are enough data on the electronic structure of $SrTiO_3$ in the literature, much less information on the electronic structure of other members of $Sr_{n+1}Ti_nO_{3n+1}$ family is available. Therefore, it is necessary to make a systematic study on the atomic and electronic properties for various layered perovskites of $Sr_{n+1}Ti_nO_{3n+1}$ ($n=1, 2, 3, \infty$). In the present work, we give our results on the structure and electronic properties of $Sr_{n+1}Ti_nO_{3n+1}$ ($n=1, 2, 3, \infty$) compounds through first principles calculations. Some of the calculated results are compared with available experimental data, and the others are given as reference to the experiments.

2. Computational details

The calculations reported herein were performed using the Vienna *ab initio* simulation package (VASP) [17,18]. The ground state of electronic structure was described within the density functional theory (DFT) using the generalized gradient approximation (GGA) [19]. The Perdew–Wang exchange correlation

* Corresponding author at: Department of Physics, Jiangxi Normal University, Nanchang 330022, China. Tel.: +86 791 8120370.
E-mail addresses: cyouyang@jxnu.edu.cn, cyouyang@hotmail.com (C.Y. Ouyang).

functional (PW91) [20] was used for the calculation of electron exchange correlations energy. The convergence tests of the total energy with respect to the K-points sampling have been carefully examined. All calculations in the present study are performed using different Monkhorst–Pack [21] K-points grids in the irreducible Brillouin zone; the final results presented in this paper are obtained with K-points grids, which ensure the K-point separation is smaller than 0.05 Å^{-1}. The electronic ground states are determined through conjugate gradient minimization of the total energy with respect to the plane wave coefficients. Energy cut-off for the plane waves is chosen to be 400 eV. Before the calculation of the electronic structure, the atomic positions, and lattice parameters are fully relaxed, the final forces on all relaxed atoms are less than 0.05 eV/Å. As all compounds studied are non-magnetic, spin polarizations are not included in all calculations, except for test purposes. The calculation of the density of states (DOS) is smeared by the Gaussian smearing method with the smearing width of 0.05 eV.

3. Results and discussion

3.1. Lattice parameters and crystal structures of $Sr_{n+1}Ti_nO_{3n+1}$ ($n=1, 2, 3, \infty$)

Fig. 1 shows a schematic view of the relaxed atomic positions of $Sr_{n+1}Ti_nO_{3n+1}$ ($n=1, 2, 3, \infty$). The $SrTiO_3$ compound has a typical perovskite cubic structure with space group (SG) Pm3m. The experimental lattice constant is 3.905 Å [22]. O, Ti, and Sr atoms occupy the face center, body center, and corner sites of the cubic unit cell, respectively.

The structure within the layer planes of $Sr_{n+1}Ti_nO_{3n+1}$ ($n=1, 2, 3$) is the same as the structure of $SrTiO_3$. The layers along the ab-plane are formed by corner-shared TiO_6 octahedron. Along the c-axis the

Fig. 1. Schematic view of the relaxed atomic structure of $Sr_{n+1}Ti_nO_{3n+1}$ ($n=1, 2, 3, \infty$) perovskite. Red, green, and grey balls are O, Sr, and Ti atoms, respectively.

thickness of each layer is n-TiO_6 octahedron thick [6]. Each layer is separated along the c-axis direction by about $a/2$ in distance with the insertion of additional O atoms, while there is a displacement of $\sqrt{2}/2a$ along the [1 1 0] direction within the ab-plane. In other words, the structure of $Sr_{n+1}Ti_nO_{3n+1}$ ($n=1, 2, 3$) is obtained in this way: from an ideal $SrTiO_3$ structure, we cut it into pieces along the c-axis direction, and the thickness of each piece is n-TiO_6 octahedron thick (when $n=\infty$, the thickness is infinitely large and thus corresponds to ideal $SrTiO_3$). Then we separate each piece with a distance of $a/2$ vertically and shift each layer horizontally by $\sqrt{2}/2a$ along the [1 1 0] direction. Finally, we add O atoms to each layer to make sure that all Ti atoms at the interface are saturated with O bonding. Table 1 gives lattice constants, space groups of the $Sr_{n+1}Ti_nO_{3n+1}$ ($n=1, 2, 3, \infty$) structures and the corresponding Ti–O bond lengths.

The theoretical lattice constants are a little larger than that of the experimental observed counterparts, because GGA calculations always over-estimate lattice constants. Because of the symmetrical atomic interaction, Ti–O bond lengths are all same within the horizontal plane (ab-plane). However, the Ti–O bond lengths along the c-axis are a little larger than that of in the horizontal plane, indication of a little expansion of the lattice along the z-direction.

3.2. Electronic properties of $Sr_{n+1}Ti_nO_{3n+1}$ ($n=1, 2, 3, \infty$)

The total density of states (TDOS) of $Sr_{n+1}Ti_nO_{3n+1}$ ($n=1, 2, 3, \infty$) are calculated and results are shown in Fig. 2. As the electronic structures of $Sr_{n+1}Ti_nO_{3n+1}$ are dominated by the TiO_6 octahedral [12], we do not observe much difference among them.

Fig. 3 shows the orbital projected density of states (PDOS) for $SrTiO_3$. There are some occupied orbits under the Fermi energy for Ti-3d and some vacant orbits above the Fermi energy for O-2p. Recognizing that the valence electronic structure of Ti atom is $3d^2 4s^2$ and the oxidation state of Ti in $SrTiO_3$ is +4, we are not expecting any Ti-3d states under the Fermi Level. The appeared states under Fermi level indicate that Ti does not complete +4 in $SrTiO_3$. At the same time, the valence electronic structure of O atom is $2s^2 2p^4$, and becomes a fully occupied state O^{2-} by accepting 2 electrons. Those unoccupied states above the Fermi level shown in Fig. 3 indicate that O in $SrTiO_3$ is not completely O^{2-}. These results show that Ti–O bond in $SrTiO_3$ is not completely ionic, some covalent feature is there. This phenomenon is similar to other oxides like gamma-Al_2O_3, whose bonding nature is also ionic dominated, but a certain covalent feature is not negligible [28]. We mention here that those states are not images from nearby atoms. In order to
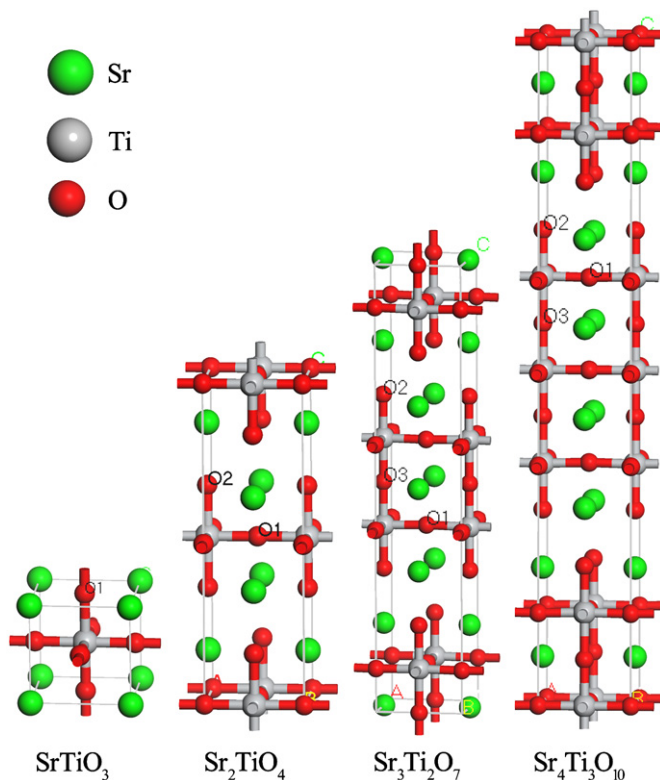
Table 1

The lattice constants (in Å), space groups (SG) and Ti–O bond lengths (in Å) of the relaxed $Sr_{n+1}Ti_nO_{3n+1}$ ($n=1, 2, 3, \infty$) systems.

	a		c		SG	Bond length	
	Cal.	Exp.	Cal.	Exp.			
$SrTiO_3$	3.912	3.905 [22] 3.898[23]	–	–	Pm3m	Ti–O1	1.956
Sr_2TiO_4	3.917	3.884[24]	12.729	12.6[24]	I4/mmm	Ti–O1	1.958
						Ti–O2	2.022
$Sr_3Ti_2O_7$	3.942	3.903[25] 3.899[26]	20.459	20.372[25] 20.400[26]	I4/mmm	Ti–O1	1.971
						Ti–O2	1.979
						Ti–O3	1.990
$Sr_4Ti_3O_{10}$	3.945	3.9 [27]	28.335	28.1[27]	I4/mmm	Ti–O1	1.973
						Ti–O2	1.970
						Ti–O3	1.973