



# Electronic and dielectric properties of Ruddlesden–Popper type and Magnéli type $\text{SrTiO}_3$



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## ABSTRACT

We have investigated the electronic and dielectric properties of the  $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$  (Ruddlesden–Popper, RP) Sr-rich and  $\text{Sr}_n\text{Ti}_{n+1}\text{O}_{3n+2}$  (Magnéli, M) Ti-rich phases of  $\text{SrTiO}_3$  using the LDA and HSE06 first principles methods. The calculated densities of states indicate that the width of band gap decreases monotonically with increasing  $n$  in the RP phases, but increases with  $n$  in the M phases. In contrast to the M phases, the RP phases exhibit better tunable dielectric properties with variations in  $n$  and also have lower dielectric loss than  $\text{SrTiO}_3$  in the lower energy range. In the case of  $n = 1$ , the real and imaginary parts of the dielectric functions of both the RP and M phases are remarkably different from stoichiometric  $\text{SrTiO}_3$  due to rumpling of the interfaces between the SrO or  $\text{TiO}_2$  bilayers and the abnormal hybridization of the Ti 3d and O 2p orbitals. The optical dielectric constant  $\epsilon_1(0)$  increases with decreasing Sr/Ti ratio, meaning that Ti-rich M phases give higher optical dielectric constants than Sr-rich RP phases. For M phases, planar defects are formed by edge-sharing  $\text{TiO}_6$  octahedra and interface rumpling of  $\text{TiO}_2$  bilayers caused by displacements of O atoms normal to the interface that create distorted octahedra. These distortions produce a crystal field that gives rise to atypical electron transfers between the Ti and O atoms within these octahedra that significantly influence the structural stability and dielectric properties of the M phases.

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## 1. Introduction

As a typical  $\text{ABO}_3$  perovskite compound,  $\text{SrTiO}_3$  (STO) has been widely used as a substrate for perovskite oxide thin films [1,2], as an alternative gate oxide for tunable dielectric devices [3], and as a photocatalyst [4]. STO can accommodate small deviations from nominal cation stoichiometry ( $0.995 < \text{Sr/Ti} < 1.002$ ) and remain a single cubic-phase perovskite [5]. However, various experiments have demonstrated that adjusting laser fluence or deposition geometry during pulsed laser deposition (PLD) results in Sr- or Ti-rich Sr–Ti–O compounds [6–10], and produces the strontium rich  $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$  Ruddlesden–Popper (RP) phase [11,12] and the titanium rich  $\text{Sr}_n\text{Ti}_{n+1}\text{O}_{3n+2}$ , Magnéli (M) phase [13]. These Sr- and Ti-rich phases are formed by inserting additional SrO- and  $\text{TiO}_2$  layers into the normal SrO– $\text{TiO}_2$  stacking of stoichiometric STO which leads to a reduction of the lattice symmetry. While bulk STO crystallizes into the high symmetry cubic space group  $Pm\bar{3}m$

[14],  $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$  (tetragonal, space group  $I4/mmm$ ) and  $\text{Sr}_n\text{Ti}_{n+1}\text{O}_{3n+2}$  (orthorhombic,  $Cmmm$ ) form lower symmetry crystal structures. Both RP and M phases with  $n = 1, 2$ , and 3 are shown in Fig. 1 which shows that both the RP phases and M phases become stoichiometric  $\text{SrTiO}_3$  as the  $n$  approaches  $\infty$ .

The layered RP oxides exhibit a rich range of inherent properties and consequently continue to be of intense interest for both their fundamental physics and technical applications [15–18]. Lee et al. successfully used molecular beam epitaxy (MBE) to fabricate the RP homologous series and observed that this class of oxide materials exhibit high film tunability combined with low dielectric loss over a broad operational frequency range (1 kHz to 125 GHz) [16,17]. The lattice parameters and band gap of the  $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$  phase can be tuned by varying  $n$ , which enables Sr–Ti–O compounds to be designed specifically for ferroelectric, photovoltaic and photocatalytic applications [16]. RP phase ( $n = 1$ ,  $\text{Sr}_2\text{TiO}_4$ ) films with well-ordered SrO double layers have been successfully fabricated by using pulsed laser deposition (PLD) [7]. This compound exhibits several potential advantages over STO, such as its closer lattice match to Si, larger band gap and lower thermodynamic driving force for reaction with Si [19,20]. The first five members

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of the  $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$  RP homologous series have been grown by reactive MBE and the dielectric measurements indicate that the dielectric constant tensor coefficient rises with increasing  $n$  [19]. Orloff et al. conducted a systematic investigation of the RP phases formed in the fabrication of Sr–Ti–O materials to determine their detailed atomic structures as well as the electronic, magnetic and optical properties of the secondary phases, and whether these phases provide a new class of tunable materials which have decreased loss, yet still retain many of the characteristics that make STO so useful [21].

Depositing the RP homologous series demonstrates the feasibility of fabricating electronically tunable microwave devices [22]. Demonstration of ordered structures of the Ti-rich M series has been more challenging. Some authors have suggested that  $\text{TiO}_2$  crystallographic shear is difficult to observe [23], and that Ti-rich STO films possess disordered structures rather than the ordered structure of the M phase [24]. However, other researchers have found that pure M phases can be formed as an accommodation mechanism for excess  $\text{TiO}_2$  in STO [6], and experimental observations have demonstrated that ordered M phase  $\text{SrTi}_2\text{O}_5$  films [25], and  $\text{Sr}_2\text{Ti}_3\text{O}_8$  films [6] were successfully deposited by reactive MBE or PLD. Adding the M phase to STO can influence the optical and electronic performance of perovskite materials. For example, it has been suggested that M phases may block the reaction pathways at phase boundaries in STO solid oxide fuel cell anodes, leading to reduced electrocatalytic activity of the anode [26].

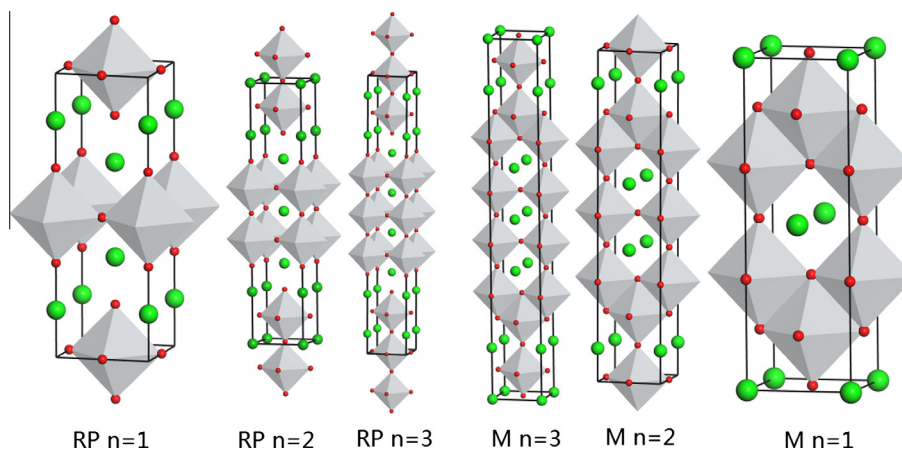
Density functional theory (DFT) [27–30] methods and atomistic simulations employing various sets of empirical pair potentials [18] have previously been used to investigate the RP perovskites. For example, DFT was used to investigate the structural stability and dielectric behavior of  $\text{Sr}_2\text{TiO}_4$  (RP phase) [27],  $\text{Sr}_4\text{Ti}_3\text{O}_{10}$  (RP phase) and  $\text{Sr}_3\text{Ti}_4\text{O}_{11}$  (M phase) [28]. Furthermore, the electronic structures and optical properties of  $\text{Sr}_2\text{MO}_4$  layered perovskites with  $M = \text{Ti}, \text{V}, \text{Cr}, \text{and Mn}$  were studied using the generalized gradient approximation (GGA) and GGA + U [29] DFT methods. Another study focused on determining the frequency-dependent optical properties of the RP series compounds ( $n = 1, 2, 3$ ) using the local density approximation (LDA) DFT method [30]. However, few theoretical studies have systematically investigated the interfacial chemistry or the optical or dielectric properties of the RP and M phases. Our aim in this contribution is to use first principles calculations of the atomic and electronic structures of the two phases to provide a deeper fundamental understanding of the optical and dielectric properties of Sr–Ti–O compounds and to determine how these properties can be tuned by changing the value of  $n$  to enable

the design of materials with specific properties for applications that exploit these attributes.

## 2. Computational details

In this paper we performed first principles local density approximation (LDA) calculations based on the Ceperly and Alder Perdew and Zunger (CA-PZ) exchange–correlation function using the CASTEP code [31]. The wave functions were expanded in plane-waves with a cutoff energy 380 eV while ultrasoft pseudopotentials were used to limit the size of the plane-wave expansion [32]. In the present calculations, the Sr  $4s^2 4p^6 5s^2$  electrons, O  $2s^2 2p^4$  electrons and Ti  $3s^2 3p^6 3d^2 4s^2$  valence electrons were treated explicitly.  $k$  point expansions of 54  $k$  points for RP phases and 64  $k$  points for M phases were determined using the Monkhorst–Pack scheme. Wave functions were optimized self-consistently and considered converged only when the energy difference between two iterations fell below  $2.0 \times 10^{-5}$  eV/atom. Geometry optimizations were converged when forces on the atoms fell below 0.05 eV/Å. The maximum stress and maximum displacement tolerances were set as 0.05 GPa and 0.002 Å, respectively.

The two series of supercell models for the RP and M phases are illustrated in Fig. 1. The  $c$  lattice vector of the supercells is parallel to  $z$ -axis. SrO bilayers are incorporated into the normal stacking of the STO crystal to form SrO–SrO (001) bilayer interfaces. The RP phase is composed of two distinct structural units—the rock salt SrO structure and the perovskite STO structure. The  $\text{TiO}_2$  bilayer structure was first observed in reduced rutile  $\text{TiO}_2$ , where their formation eliminates oxygen vacancies to leave  $\text{Ti}^{3+}$ -rich shear planes [28]. When  $\text{TiO}_2$  bilayers emerge in the normal stacking of STO, M phases containing two distinct structural units, the rutile  $\text{TiO}_2$  and the perovskite STO, are formed. In the present paper, we first optimized the crystal structures of supercell models of the RP and M phases. We have found that the in-plane lattice constants of RP or M phases change only slightly with the index  $n$  and are similar to our calculated lattice parameter of bulk STO of 3.86 Å. However, the  $c$ -axis lattice constant of both the RP and M phases is sensitive to  $n$ . For the RP phase the  $c$ -axis lattice constant expands by 6.7% ( $n = 1$ ), 3.9% ( $n = 2$ ), and 2.6% ( $n = 3$ ), while for M phase the  $c$ -axis lattice constant expands by 4.4% ( $n = 1$ ), 2.8% ( $n = 2$ ), and 2.1% ( $n = 3$ ). As these results show, the  $c$ -axis lattice expansion of RP phases is larger than that of the M phases. In the M phases, the perfect  $\text{TiO}_6$  octahedra chains in the [001] direction are disrupted by incorporation of  $\text{TiO}_2$  bilayers and the  $1/2[001]$  lattice misfit



**Fig. 1.** Supercell models of the  $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$  Ruddlesden–Popper series and  $\text{Sr}_n\text{Ti}_{n+1}\text{O}_{3n+2}$  Magnéli series ( $n = 1, 2, 3$ ). Green and red spheres represent Sr and O atoms, respectively. Ti atoms reside at the centers of octahedra of O atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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