Structural, electronic and optical properties of cubic SrTiO$_3$ and KTaO$_3$: *Ab initio* and GW calculations

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ABSTRACT

We present first-principles VASP calculations of the structural, electronic, vibrational, and optical properties of paraelectric SrTiO$_3$ and KTaO$_3$. The *ab initio* calculations are performed in the framework of density functional theory with different exchange-correlation potentials. Our calculated lattice parameters, elastic constants, and vibrational frequencies are found to be in good agreement with the available experimental values. Then, the bandstructures are calculated with the GW approximation, and the corresponding band gap is used to obtain the optical properties of SrTiO$_3$ and KTaO$_3$.

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1. Introduction

ABO$_3$ perovskites have a variety of physical properties which are strongly dependant on their chemical composition. In some cases, they show various phase transitions, including sometimes a transition from a paraelectric to a ferroelectric compound. In the paraelectric phase, the structure of ABO$_3$-like perovskites is simple: it is a cubic structure with A at the corners, B at the center and O at the face centers. This simple structure can be seen as BO$_6$ octahedrons with A between the octahedrons. The Wyckoff positions of the atoms are 1a (A), 1b (B) and 3c (O) [1]. The properties of perovskites oxides are temperature, hydrostatic, electromagnetic and environment sensitive, with high dielectric constant and low loss answer. All these macroscopic quantities are usually coupled. Consequently, they have very important engineering applications from telecommunication to cryogenic and many promising applications can be found in electrochemistry [2–8]. The study of the oxygen-octahedral ferroelectrics crystal has not stopped since 1942 until today [9]. The study usually concerns electrical, mechanical, optical or thermodynamic properties by experimental measurements or by computations.

Most of the time, these materials have an unexpected behavior and theoretical studies are needed for a better comprehension and to predict new materials with specific properties for particular applications. First-principles calculations using Density Functional Theory (DFT) within different approximations have been used to characterize these materials [2–8,10,11], but much remain to be done in order to fully understand this class of material.

In the present study, we consider two lead-free materials: SrTiO$_3$ (STO) and KTaO$_3$ (KTO). Their chemistry is quite different since they have different type of d electrons for the metal B atom (3d for STO and 5d for KTO), and belongs to two different groups for the A atoms (IA and IIA), the first one being monovalent and the second being divalent. While KTaO$_3$ remains in a cubic phase independently of the temperature, SrTiO$_3$ has a structural phase transition at 110 K which reduces the symmetry from cubic to tetragonal. Here we will focus only on the cubic phase.

Our paper is organized as follows: in the next section, we describe our first-principles calculations details, in Section 3 the theoretical approach for the optical properties is presented, in Section 4 we present our results concerning their structural, electronic and optical properties and discuss them in comparison with previous calculations and experimental results, and finally our conclusions are presented in Section 5. Notice that Evarestov et al. [12] have studied the cubic and tetragonal phases of STO and

compared the results obtained with an atomic orbital code and a plane wave code. However, the study made with the plane wave code was done with the PBE and PBE0 functionals, and is therefore different from the study presented here (see below).

2. Theory and computational details

Our calculations have been performed with the Vienna *Ab initio* Simulation Package [10,11] implementing the projector augmented wave method [13]. For the structural properties, we have used density functional theory [14,15] with various exchange-correlation potentials such as the generalized gradient approximation of Perdew–Burke–Ernzerhof [16], PBEsol [17,18], and HSE [19]. To ensure convergence, the plane-wave cut-off was set to 500 eV and the k-points mesh to $18 \times 18 \times 18$. Using this setup, we have calculated the structural properties (see below), including the elastic constants and the phonon frequencies at the Γ point. The elastic tensor for the Pm-3m structure is reduced to three elements C_{11}, C_{12} and C_{44}, and the stability conditions for a cubic structure are: $C_{11} > 0$, $C_{44} > 0$, $C_{11} - C_{12} > 0$ and $C_{11} + 2C_{12} > 0$ [20]. The phonon frequencies have been obtained by the calculation of the Hessian matrix, knowing that a crystal structure is considered stable if all its phonon frequencies are real [21].

We have also performed GW calculations [22–24] to obtain realistic values of the band gaps. With this approximation, the exchange-correlation potential is replaced by a non-local and energy dependent self-energy which allows to obtain excited states. In this case, a quasiparticle equation is solved, written as follows:

$$(T + V_{ext} + V_h)\psi_{\mathbf{k}n}(\mathbf{r}) + \int d^3 r' \Sigma(\mathbf{r},\mathbf{r}',E_n(\mathbf{k}))\psi_{\mathbf{k}n}(\mathbf{r}') = E_n(\mathbf{k})\psi_{\mathbf{k}n}(\mathbf{r})$$

where T is the free-electron kinetic energy operator, V_{ext} is the external potential due to the ion cores, V_h is the Hartree potential, Σ is the self-energy operator, and $E_n(\mathbf{k})$ and $\psi_{\mathbf{k}n}(\mathbf{r})$ are, respectively, the quasiparticle energy and wave function. Then Σ is approximated by the product of the Green's function G and the screened Coulomb interaction W, which leads to the GW approximation. During our calculations, a cut-off of 250 eV was used for the polarisability matrix, and 500 bands were used for the summation over the conduction states (see Ref. [25] for the details of the implementation of the GW approximation in VASP).

To study the optical properties, we calculated the frequency-dependent dielectric matrix in the long wavelength limit $(q=0)$ using the sum over states approach. In this case, the formula for the imaginary part of the dielectric function is:

$$\epsilon_2(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q \to 0} \frac{1}{q^2} \sum_{c,v,k} 2\omega_k \delta(\epsilon_{ck} - \epsilon_{vk} - \omega) \langle u_{ck+q} | u_{vk} \rangle \langle u_{ck+q} | u_{vk} \rangle^*$$

where the indices c and v correspond to the conduction and valence band states, respectively and u_{ck} is the periodic part of the orbitals at the k-point k.

Then, the real part $\epsilon_1(\omega)$ of the frequency-dependent dielectric function can be derived from the imaginary part using the Kramers–Kronig relations:

$$\epsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \epsilon_2(\omega')}{\omega'^2 - \omega^2 + i\eta} d\omega'$$

To converge our optical spectra, we have used a $30 \times 30 \times 30$ k-point mesh and the imaginary part of the dielectric function has been corrected by using the GW approximation (see below).

3. Results and discussion

3.1. Structural properties

To study the structural properties of SrTiO$_3$ and KTaO$_3$, we calculated the total energy for different volumes around the equilibrium cell volume. Then, the calculated total energies are fitted to a third-order Murnaghan equation of state [26] to determine the equilibrium lattice constant a_0, the bulk modulus B_0, and its pressure derivative B'. The corresponding results are presented in Table 1 together with the experimental data as well as results of previous first-principle calculations conducted using the PBE functional. It appears that the PBEsol and HSE functionals performs very similarly for a_0, B_0, and B', obtaining a very good agreement with the available experimental values while PBE is slightly less good [27], with for instance an equilibrium lattice parameter too long by about 0.04 Å for both STO and KTO. In the same way, the bulk modulus and its derivative obtained with the PBEsol functional ($B_0 = 185.1$ GPa and $B' = 5.2$ for STO and $B_0 = 202.4$ GPa and $B' = 4.5$ for KTO) are close to the values obtained with HSE ($B_0 = 196.0$ GPa and $B' = 5.2$ for STO and $B_0 = 211.2$ GPa and $B' = 4.5$ for KTO) while the PBE values ($B_0 = 168.8$ GPa and $B' = 4.4$ for STO and $B_0 = 187.1$ GPa and $B' = 5.9$ for KTO) are somehow different. In this case, the bulk modulus obtained with PBE is closer to the experimental value ($B_0 = 171.6$ GPa for KTO and $B_0 = 212.3$ GPa for STO) but the bulk modulus derivative is different ($B' = 5.25$ for STO while the experimental value for KTO is unknown). The analysis is more complicated for the elastic constants with none of the three functionals giving a perfect agreement with experiments, but all of them providing reasonable values (see Table 1 for the details) in comparison with experiments.

In Table 2, we present our calculated phonon frequencies at the center of the Brillouin zone (Γ). We do not report the value for the silent mode since there are no experimental value to compare

Table 1
Calculated values of lattice parameter a_0 (in Å), equilibrium bulk modulus B_0 (in GPa), the pressure derivative of the bulk modulus B' and the elastic constants (in GPa).

Method	PBE	PBESol	HSE	Others (PBE)	Experimental
STO					
a_0	3.95	3.90	3.90	3.93 [27] 3.94 [12]	3.898 [35]
B_0	168.8	185.1	196.0	171 [27] 169 [12]	171.6 [34]
B'	4.4	5.2	5.2		5.25 [34]
C_{11}	318.6	355.5	406.4	319.3 [27]	317.0 [27]
C_{12}	99.3	105.2	129.6	97.5 [27]	102.5 [27]
C_{44}	109.8	114.4	145.0	113.0 [27]	123.5 [27]
KTO					
a_0	4.04	4.00	4.00	3.95 [37]	3.9885 [36]
B_0	187.1	202.4	211.2	230 [37]	212.3
B'	4.6	4.5	4.5	3.69 [37]	
C_{11}	416.5	451.2	520.6	440.7 [37]	431.0 [42]
C_{12}	78.3	81.1	107.3	65.6 [37]	103.0 [42]
C_{44}	100.9	102.5	131.1	85.6 [37]	109.0 [42]

Table 2
Calculated phonon frequencies of STO and KTO (cm^{-1}).

Method	PBE	PBESol	HSE	Others	Experimental
STO					
TO1	132i	i69	109i	68i [38] 133i [12]	91 [40]
TO2	144	157	161	162 [38] 146 [12]	175 [40]
TO3	508	533	532	549 [38] 508 [12]	543 [40]
KTO					
TO1	75i	67	51i		25 [41]
TO2	188	191	203		196 [41]
TO3	499	521	527		547 [41]