Understanding electronic and optical properties of strontium titanate at both PBE and HSE06 levels

Jianhui Yang, Qiang Fan

School of Physics and Electronic Engineering, Leshan Normal University, Leshan, 614004 P. R. China

E-mail: yjh20021220@foxmail.com

Abstract. The structural parameters, electronic structure and optical properties of strontium titanate have been investigated by the first-principles. Exchange–correlation effects are treated by the generalized gradient approximation(GGA) employing Perdew–Burke–Ernzerhof (PBE) functional and hybrid density functional Heyd-Scuseria-Ernzerhof(HSE06). The direct-band gaps are equal to 2.06 and 3.73 eV under PBE and HSE06 level, respectively. The indirect-band gaps are equal to 1.67 and 3.33 eV under PBE and HSE06 level, respectively. The optical properties including complex dielectric function, absorption coefficient, refractivity and reflectivity index have been calculated. Meanwhile, the origin of the spectral peaks on the basis of the electronic band structures has been interpreted.

1. Introduction

Strontium titanate (SrTiO₃ or STO for short) has cubic structure and space group Pm₃m stable from 23 to 1100°C with wide band gap (~3.3 eV) and large dielectric constant (300) [1-2]. As a chemistry and thermally stable ceramic oxide, which is widely studied due to the important applications in ferroelectricity[3], thermoelectricity[4-9], photoelectricity[2], superconductivity[10], semiconductivity [11-12], photoconductivity [13-14], microelectronics [15] and so on. Recently, cubic STO are widely studied as a promising optical material, such as photoluminescence emission and rear-earth doped cubic STO phosphors, which significantly attracted material scientists due to the enhanced luminescence properties [16-19]. However, so far, most of the works have been addressed from experiment; we undertake a theoretical study to learn more about it in this paper. We investigate the electronic and optical properties of the cubic structures of the perovskite STO. First, we calculate the electronic structures, because the optical properties depend on the electronic transitions between occupied bands and empty bands. Second, we calculate the optical properties, including complex dielectric function, absorption coefficient, refractive index and reflectivity.

The reliable optical property is decided by accurate electronic structure. Band gap is very challenging for first principle theory, since most methods, including local density approximation (LDA) and generalized gradient approximation (GGA), the common exchange–correlation functional in the density functional theory (DFT), sometimes underestimate band gap by as large as 3 eV compared with the experimental results [20-22]. Hybrid functional, which mixes Hartree-Fock exchange functional with LDA or GGA exchange-correlation functional, can provide decent prediction for band gap [23-24]. In this paper, we are presenting a detailed investigate for STO on the electronic structure and optical properties using the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional based on DFT rather than the scissors operator for standard DFT functional, to obtain
accurate and reliable optical properties for STO system. To compare the effect of electronic and optical properties by hybrid function, the GGA of DFT employing Perdew–Burke–Ernzerhof (PBE) functional form has been chose as well.

2. Method of calculation

All calculations in our work were performed based on the DFT within the projector augmented wave (PAW) method as implemented in the Vienna Ab-initio Simulation Package (VASP) code [25-26]. The structure optimization was performed using the GGA of DFT employing PBE functional form [27]. The electronic structures and optical properties were calculated on the optimized structures using the hybrid density functional HSE06, which replaces the slowly decaying long-ranged part of the Fock exchange, by the corresponding density functional counterpart. The resulting expression for the exchange-correlation energy is given by:

\[
E_{\text{XC}}^{\text{HSE}} = aE_{\text{X}}^{\text{HF,SR}}(\omega) + (1-a)E_{\text{X}}^{\text{PBE,SR}}(\omega) + E_{\text{X}}^{\text{PBE,LR}}(\omega) + E_{\text{C}}^{\text{PBE}}
\]

where, the screening parameter \(\omega\) defines the range-separation of the electron–electron interaction into a short-(SR) and long- ranged (LR) part, is assigned a value of 0.207\(\text{Å}^{-1}\) [28]. The short-range interactions become negligible when the distance exceeds 2/\(\omega\). Hartree-Fock mixing constant \(\alpha\) is set to 0.28.

The valence electron for the Sr, Ti, O atoms were chosen as 4s^24p^55s^2, 3p^63d^34s^2, and 2s^22p^4, respectively. Monkhorst-Pack grids of 11×11×11 was used for Brillouin zone sampling. The electron wave function was expanded in plane waves to a cutoff energy of 450 eV with total energy converging to lower than 1×10^{-5} eV. The lattice constants and all atomic positions for supercell were fully relaxed until the maximal force on each atom was less than 0.01 eV/Å. The higher cutoff energies and more k-points have been chosen and the results barely changed, which is in accordance with other theoretical calculations [15-29-30].

3. Results and discussion

The optimized lattice constants are \(a = b = c = 3.945 \text{ Å}\) for STO, which are in good agreement with the experimental and theoretical data [29, 31, 32]. The result shows that the calculation parameters are reasonable. As well known, electronic transport and optical properties of semiconductors are dominated by the electronic structures. Thus, it is necessary to understand the nature of the electronic structures before explaining and optimizing the properties of the systems. In the band structure calculation, a path along higher symmetry points \(\Gamma(0, 0, 0)-X(0, 0.5, 0)-M(0.5, 0.5, 0)-\Gamma(0, 0, 0)-R(0.5, 0.5, 0.5)-X(0, 0.5, 0)\) has been chosen in the first Brillouin zone. The calculated band structure along higher symmetry direction in the Brillouin zone of pure STO using PBE and HSE06 are shown in figure 1.
As shown in figure 1, for pure STO, the calculated band structure shows that the indirect ($\Gamma \rightarrow R$) band gap energies are 1.67 and 3.33 eV for PBE and HSE06, respectively. The direct ($\Gamma \rightarrow \Gamma$) band gap energies are 2.06 and 3.73 eV for PBE and HSE06, respectively. Compared with the energy band of PBE, the conduction band minimum (CBM) of HSE06 move into high energy range. Meanwhile both the indirect and direct band gap energies of PBE are smaller than that of HSE06. The results of HSE06 are in excellent agreement with experimental results [1-2], which means HSE06 hybrid density functional can truly predict the electronic structure for pure STO.

More detail property about the electronic structure can be observed from the partial and total DOS. The partial DOS (PDOS) from PBE and HSE06 functional are shown in figure 2(a) and figure 2(b). In figure 2(c) the total DOS (TDOS) is plotted as well.

Figure 1. Band structure of pure STO (The Fermi level is set at 0 eV).

Figure 2. Partial (PDOS), local (LDOS), and total (TDOS) densities of states of cubic STO.

From the TDOS curves figure 2, it is obvious that the valence band maximum (VBM) and conduction band minimum (CBM) are contributed mainly by O-2p states and Ti-3d states, respectively. Comparing with PBE level results, the conduction band of HSE06 moves into higher energy range and the valence band moves into lower energy range, which makes the energy band of HSE06 larger than that of PBE. Valence band (VB) of HSE06 can be divided into three parts: firstly, from -19.61 to
-18.04 eV is mostly formed by O-2s states; secondly, range from -16.08 to -15.23 eV, resulting from Sr-4p; thirdly, between -5.07 to 0 eV is formed by O-2p states with slight admixture of Ti-3d. As regards for the conduction band (CB), can be assigned to Ti-3d states with some admixture of O-2p states.

It is known that the optical properties can be calculated by the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of the dielectric function, respectively. The imaginary part $\varepsilon_2(\omega)$ is a critical characteristic of the optical properties for all the optical materials which is related to energy loss of electric field in solid. In general, the electronic structure is directly associated with imaginary part $\varepsilon_2(\omega)$ and it can be calculated by adding all possible occupied states to the unoccupied states of transitions. The imaginary part of the dielectric function $\varepsilon_2(\omega)$ of the pure STO at both PBE and HSE06 levels, are shown in figure 3 with energy up to 50 eV.

![Figure 3. The imaginary part of dielectric function for cubic STO.](image)

It can be seen clearly from figure 3, For pure STO, there are three main peaks. The energy threshold for PBE level is 2.09 eV, according with the direct band gap energy. The first peak of PBE functional is at 4.03 eV, which mainly be caused by optical transitions between O-2p states in the highest valence band and Ti-3d states in the lowest conduction band. The second peak at 22.50 eV corresponds to transfers from the Sr-4p valence bands to the Ti-3d conduction bands. The peak at 36.50 eV corresponds to the deep electron excitations from Sr-4p, Ti-3d to the conduction bands.

Compared with the imaginary part of dielectric function of PBE, the results of HSE06 have same tendency, also have three mainly peaks. The most remarkable difference for imaginary part of dielectric function of PBE and HSE06 is the curve moving into higher energy and the energy threshold for HSE06 level is 3.79 eV. There are three main peaks at 6.00, 25.41 and 41.45 eV which have a good agreement with the previous report [33] due to the conduction band of Ti-3d moving into higher energy.

The real part $\varepsilon_1(\omega)$ can be derived from the imaginary part using the Kramers–Kronig transformation [34] and the optical properties such as refractivity index ($n(\omega)$), reflectivity($R(\omega)$) index, and absorption coefficient $\alpha(\omega)$ can be derived from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$. In this paper, the absorption coefficient $\alpha(\omega)$ calculated using the relation as follows.

$$\alpha(\omega) = \sqrt{2\omega} \left[ \sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) - \varepsilon_1(\omega)} \right]^{3/2}$$  (2)
\[ n(\omega) = \left( \frac{\varepsilon_r^2(\omega) + \varepsilon_i^2(\omega) + \varepsilon_s(\omega)}{2} \right)^{1/2} \]  

\[ R = \frac{\sqrt{\varepsilon(\omega) - 1^2}}{\sqrt{\varepsilon(\omega) + 1}} \]  

For the promising applications in optoelectronic devices, the optical absorption should be taken into account, the absorption coefficients, refractivity, reflectivity index of pure STO under PBE and HSE06 levels are plotted in figure 4.

**Figure 4.** The absorption coefficients refractivity, reflectivity index for pure STO.

As can be seen from figure 4, the curves of absorption coefficients refractivity and reflectivity index are similar between PBE and HSE06 levels. The absorption, refractivity and reflectivity peaks moves into higher energy range as the tendency of dielectric function. The absorption thresholds for PBE and HSE06 levels of pure STO are at 2.09 and 3.79 eV, which is determined by the transition between VBM and CBM as same with dielectric function. The absorption coefficient for pure STO is low in the visible region.

4. **Conclusion**

In this work, the electronic structure and optical properties of pure STO have been systematically investigated using first-principles calculations based on DFT. The calculated band structure shows that the indirect (\(\Gamma\rightarrow R\)) and direct (\(\Gamma\rightarrow \Gamma\)) band gap energies are 3.33 eV and 3.73 eV, respectively for Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional, which are in excellent agreement with experimental results. The results show that HSE06 corrects the shortcomings of standard Perdew–Burke–Ernzerhof (PBE) approximation for band structure and truly predict the electronic structure for pure STO. We conclude that the accurate and systematic description of the electronic, optical and mechanical properties of such type of materials can be achieved with the use of HSE06. We hope that our work will provide a comprehensive understanding of perovskite STO, and provide assistance and guide to design and development of such type of materials, which are very important for the industrial and scientific point of view.

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