

STRUCTURAL, ELECTRONIC AND OPTICAL PROPERTIES STUDY OF BROOKITE TiO₂

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ABSTRACT

Structural, electronic and optical properties of titanium dioxide (TiO₂) in brookite phase are studied via first-principles calculations in the framework of density functional theory (DFT). The exchange-correlation functional from local density approximation (LDA) and generalized gradient approximation (GGA) are used to calculate the properties of brookite TiO₂. The structural parameters of brookite in orthorhombic structure (*Pbca* space group) are well agreed with the previous experimental report. The obtained direct band gaps from the top of valence band to the bottom of conduction band from GGA are slightly higher than LDA and underestimate the experimental band gap. The density of states and atomic population show the Ti-O bonding character and distribution of electrons in brookite. The dielectric function is also analyzed together with other optical properties such as dielectric function, refractive index, loss function, reflectivity and absorption coefficient. Thus, the first-principles calculations of brookite can provide understanding about its properties using different exchange-correlation functional from LDA and GGA.

Keywords: First-principles; Density functional theory (DFT); Brookite; Electronic; Optical;

INTRODUCTION

Titanium dioxide (TiO_2) exists in three natural phases, which are rutile, anatase and brookite. Rutile is the most stable phase, whereas anatase and brookite are metastable phases and change to rutile when they are calcined at higher temperatures [1, 2]. Most of the previous studies has been focused on rutile and anatase, while brookite has been rarely used and studied because of its complicated structure and most difficult to prepare in its pure form. So far, only a few groups have reported the properties study on brookite. Consequently, the data of brookite in experimental or theoretical studies are limited compared to those on rutile and anatase. However, there has been increasing interest in brookite TiO_2 lately as it found to display remarkable properties [3].

A few studies for the preparation and characterization of both pure brookite and TiO_2 mixtures with brookite have been reported during the past years [4, 5]. Kandiel et al. investigated photocatalytic activities of brookite nanoparticles that show higher photocatalytic than anatase and a comparable activity to the anatase-rich nanoparticles. Meanwhile, the pure brookite nanoparticles have been found to exhibit higher photocatalytic activity than brookite-rich nanoparticles [6]. Recently, Manjumol et al. reported that the brookite rich titania prepared by novel aqueous sol-gel method presented superior photocatalytic activity under UV irradiation with a rate constant value of 0.011 min^{-1} compared to the value of 0.003 min^{-1} for pure rutile rich titania samples [7]. The fabricated bilayer TiO_2 film-based solar cells using brookite nanocubes as an overlayer of the anatase TiO_2 prepared by Xu et al. enhances both the open-circuit voltage and short-circuit current which significantly improved the conversion efficiency of solar cell. The tuning of the components and structure of the TiO_2 photoanode offer a new strategy for the development of dye-sensitized solar cells (DSSCs) with low-cost and high efficiency [8].

Besides experimental studies, brookite has also been studied theoretically within first-principles calculations in the density functional theory (DFT) framework. Extensive theoretical research of the solid state materials has been performed from the previous studies by employing the different method and software to calculate the properties of the materials [9-12]. A few first-principles studies on brookite TiO_2 in bulk and surfaces have been reported to describe its physical and chemical properties. In previous work, Shojaee et al. studied the electronic and dynamical properties of brookite TiO_2 [13]. The surface properties of brookite are reported by Gong et al. by investigating the structures and energetics of ten stoichiometric 1×1 low-index surfaces of brookite [14]. The structural and electronic properties of the bulk and the low-index surfaces of brookite with the response to hydrostatic pressure are studied by Beltrán et al. using the hybrid DFT calculations [15].

Thus, for a better understanding of the least studied TiO_2 in brookite phase, this paper present the first-principles calculations on structural, electronic and optical properties of brookite TiO_2 under DFT field by considering the role of exchange-correlation function from LDA and GGA as an aim to test the performance from different exchange-

correlation functional. The results of the structural parameters, band structures, partial and total density of states, atomic population, dielectric function, refractive index, loss function, reflectivity and absorption coefficient of brookite are discussed in this paper.

EXPERIMENTAL

First-principles calculations based on density functional theory plane wave pseudopotential method were performed using Cambridge Serial Total Energy Package (CASTEP) computer code [16]. Exchange-correlation functional were tested using local density approximation (LDA) by Ceperley and Adler [17] as parametrized by Perdew-Zunger [18] (CAPZ) and generalized gradient approximation (GGA) of Revised Perdew-Burke-Ernzerhof (RPBE) [19], Perdew-Wang91 (PW91) [20] and Wu and Cohen (WC) [21]. The Ti (*3s*, *3p*, *3d*, *4s*) and O (*2s*, *2p*) of brookite TiO_2 were considered as valence states. The energy cutoff of 380 eV with *k*-point of $2 \times 3 \times 3$ were selected. The geometry optimization convergence threshold for energy change, maximum force, maximum stress and maximum displacement were set for 5×10^{-6} eV/atom, 0.01 eV/Å, 0.02 GPa and 5×10^{-4} Å respectively.

RESULTS AND DISCUSSION

Crystal Structure.

The crystal structure of brookite TiO_2 (orthorhombic, space group *Pbca*) is visualized in Figure 1. The unit cell of brookite contains 24 atoms which consist of 8 titanium (Ti) atoms and 16 oxygen (O) atoms with 8 formula units in the orthorhombic cell. The brookite can be presented as TiO_6 octahedra, where Ti atom binds with six O atoms. There are different length of Ti-O bond in ranges of length from 1.850 to 2.141 Å as obtained from LDA and GGA functional. The structural parameters of brookite computed from LDA and GGA in comparison with experimental values are listed in Table 1. The calculated lattice parameters are well agreed with the experimental lattice parameters with small percentage deviation less than 1.5% and for the cell volume less than 5%. The lattice parameters from GGA-WC exhibit smallest percentage deviation which shows the good agreement with the experimental values compared to the other calculated lattice parameters from LDA, GGA-RPBE and GGA-PW91 functional.

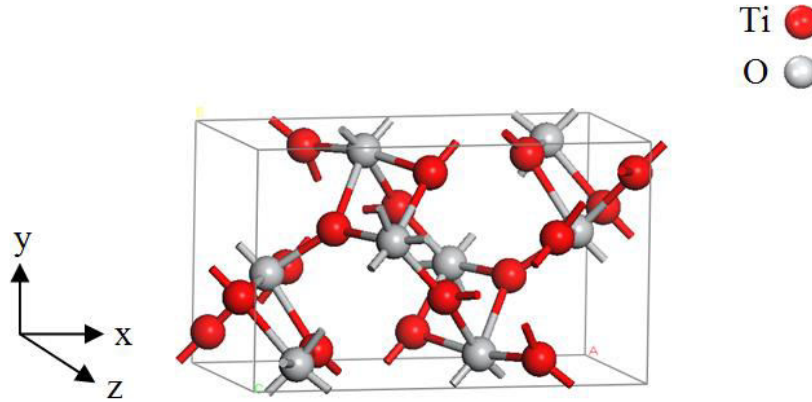


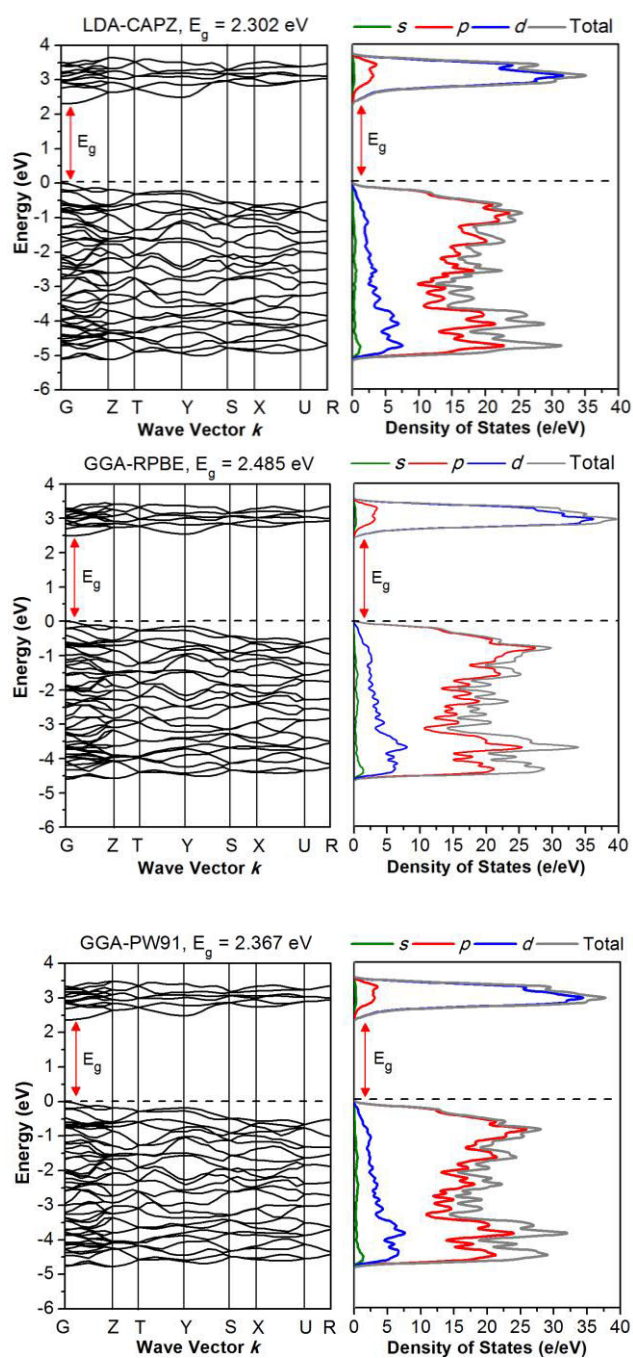
Figure 1: Crystal structures for unit cell of brookite TiO_2

Table 1: Structural parameters of brookite TiO_2 in comparison with the experimental data

Lattice Parameters	LDA	GGA			Experiment [22]
		RPBE	PW91	WC	
a (Å)	9.098 (-0.89)	9.327 (+1.60)	9.252 (+0.78)	9.182 (+0.02)	9.180
b (Å)	5.396 (-1.12)	5.565 (+1.98)	5.500 (+0.78)	5.448 (-0.16)	5.457
c (Å)	5.088 (+1.35)	5.209 (+0.99)	5.177 (+0.37)	5.135 (-0.45)	5.158
V (Å ³)	249.74 (+3.35)	270.37 (+4.63)	263.41 (+1.93)	256.84 (-0.60)	258.40

Electronic Properties.

The band structures, as well as density of states of optimized brookite TiO_2 , are presented in Figure 2. The band gap of brookite along with band dispersion from G to R is direct from the top of valence band to the bottom of conduction band at G point. The band gap from LDA, GGA-RPBE, GGA-PW91 and GGA-WC are consistent with each other which about 2.3 to 2.5 eV. The maximum of band gap at 2.485 eV is obtained from GGA-RPBE. There is an improvement in the band gap from GGA compare to LDA. However, the band gap of brookite from conventional LDA and GGA are lower than experimental band gap as previously shown in the transition metal and rare-earth metal compounds. The exchange-correlation functional from density functional theory (DFT) suffer from the well-known trend in obtaining the exact band gap compared to the experiment. The experimental band gap of brookite is about 3.13 eV as reported by Reyes-Coronado et al. [23]. Thus, the underestimation of the band gap from first-principles calculations can be fixed by using hybrids functional or Hubbard U method in order to make the band gap comparable with the experimental results [24-26].



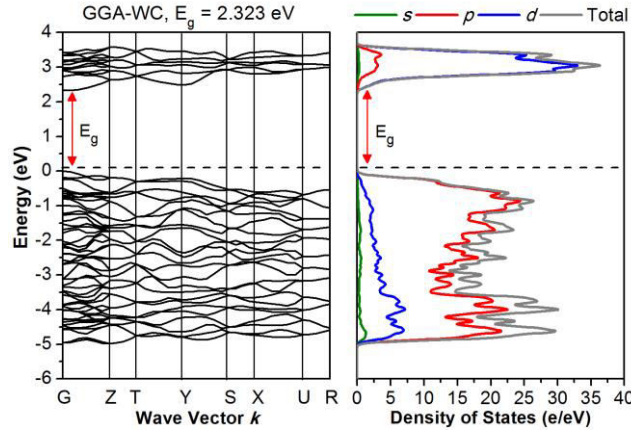


Figure 2: Band structures and density of states of brookite TiO_2

The partial and total density of states are calculated in order to identify the electrons contribution from s , p and d orbitals in brookite TiO_2 . The valence band from -6 to 0 eV show a strong hybridization between O $2p$ and Ti $3d$ electrons while the conduction band from 0 to 4 eV is mostly contributed by Ti $3d$ electrons with a small contribution from the O $2p$ electrons. Both of Ti $3d$ and O $2p$ states are involved in electron transition from the valence to conduction band across the band gap. The further exploration of the electronic properties of brookite from Ti and O atoms can be obtained from the atomic population. The partial atomic charges of Ti and O atoms from Mulliken population analysis are shown in Table 2. The results from LDA and GGA show the partial charges of about 1.23 to 1.32 e for Ti and -0.60 to -0.68 e for O. The charges are larger than +1 for Ti and less than -0.6 for O. The present net charges of Ti and O atoms indicates a charge transfer between the atoms.

Table 2: Mulliken population analysis of brookite TiO_2

Species	LDA-CAPZ		GGA					
			RPBE		PW91		WC	
	Ti	O	Ti	O	Ti	O	Ti	O
s	2.27	1.84	2.26	1.85	2.27	1.85	2.27	1.84
p	6.32	4.77, 4.79	6.29	4.79, 4.83	6.31	4.79, 4.82	6.33	4.77, 4.79
d	2.18	0	2.12	0	2.13	0	2.15	0
Total	10.77	6.60, 6.63	10.68	6.64, 6.68	10.70	6.63, 6.66	10.75	6.61, 6.64
Charge (e)	1.23	-0.60, -0.63	1.32	-0.64, -0.68	1.30	-0.63, -0.66	1.25	-0.61, -0.64

Optical Properties.

The optical properties obtained from the light passing through the material, for example, dielectric function, refractive index, loss function, reflectivity and absorption coefficient are analyzed for brookite TiO_2 . These optical properties are related with the complex dielectric function which can be defined by the following relation:

$$\begin{aligned} & \varepsilon(\omega) \\ &= \varepsilon_1(\omega) \\ &+ i\varepsilon_2(\omega) \end{aligned} \quad (1)$$

where $\varepsilon_1(\omega)$ is real part and $\varepsilon_2(\omega)$ is imaginary part. The real part is related with electronic polarizability of the material and the imaginary part is correlated to the electronic absorption of the material. The imaginary part of dielectric function can be defined as:

$$\varepsilon_2(\hbar\omega) = \frac{2\pi e^2}{\Omega\varepsilon_0} \sum_{k,v,c} |\langle \Psi_k^c | u \cdot r | \Psi_k^v \rangle|^2 \delta(E_k^c - E_k^v - E) \quad (2)$$

where e , u , Ψ_k^v and Ψ_k^c represent electronic charge, incident electric field, valence band and conduction band wave functions at k point respectively. The Kramers-Kronig relation is used to obtain the real part of dielectric function from the imaginary part. The relation of refractive index, $n(\omega)$ and extinction coefficient, $k(\omega)$ with real part are as follows:

$$n(\omega) = \sqrt{\frac{|\varepsilon(\omega)| + \varepsilon_1(\omega)}{2}} \quad (3)$$

$$k(\omega) = \sqrt{\frac{|\varepsilon(\omega)| - \varepsilon_1(\omega)}{2}} \quad (4)$$

The dielectric function, $\varepsilon(\omega)$ and refractive index, $n(\omega)$ of brookite TiO₂ up to a photon energy of 40 eV using LDA, GGA-RPBE, GGA-PW91 and GGA-WC functional are presented in Figure 3 and Figure 4 respectively. The calculated dielectric constant and refractive index in the limit of zero photon energy calculated from each functional are differ at about 4.84 to 4.90 and 2.19 to 2.22 respectively. The LDA results are slightly higher compared with other functional from GGA. The real part $\varepsilon_1(\omega)$ of the dielectric function shows the highest peak intensity at about 2.73 to 3.01 eV belongs to the electronic transition from Ti 3d to O 2p at the conduction band and valence band. The imaginary part $\varepsilon_2(\omega)$ shows the first energy peak at about 3.61 to 3.78 eV. The extinction coefficient $k(\omega)$ is the imaginary part of the refractive index, which can be related to the light absorption. The major peaks of the extinction coefficient are located at 4.26 to 4.36 eV.

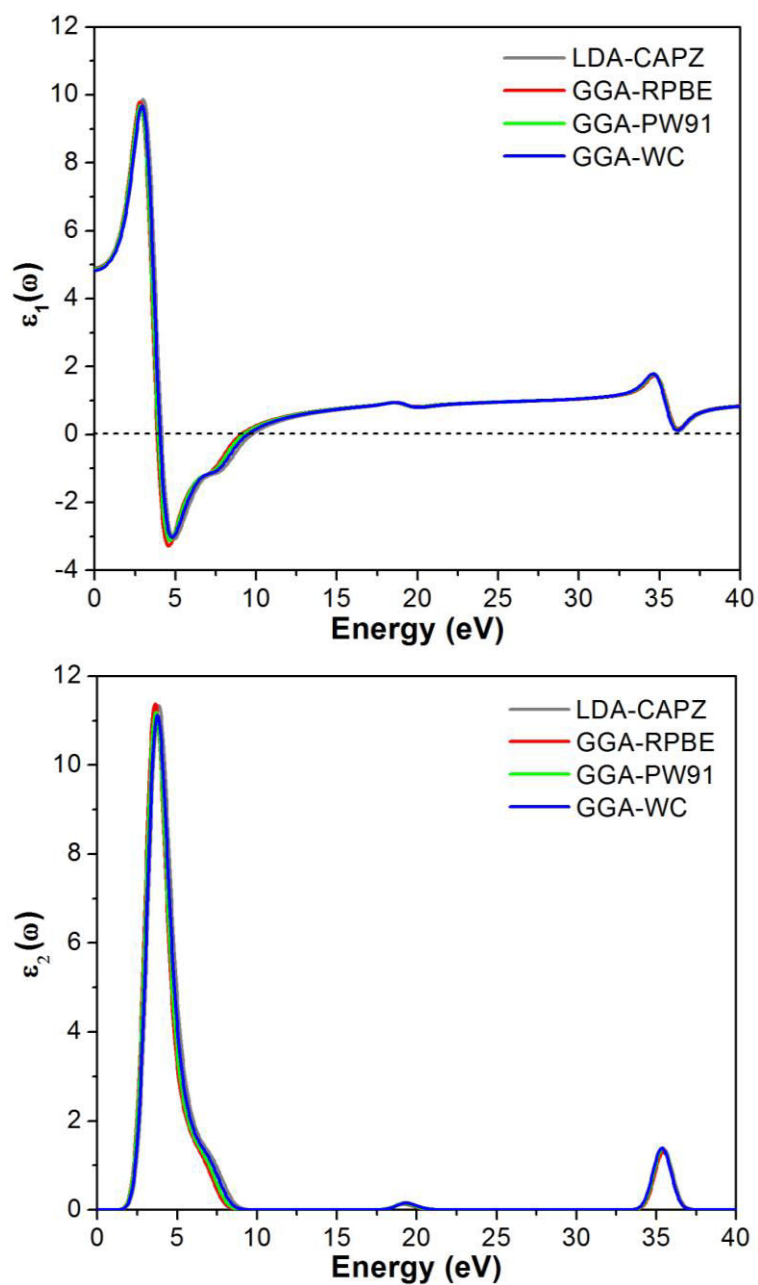


Figure 3: Real and imaginary parts of dielectric function for brookite TiO_2

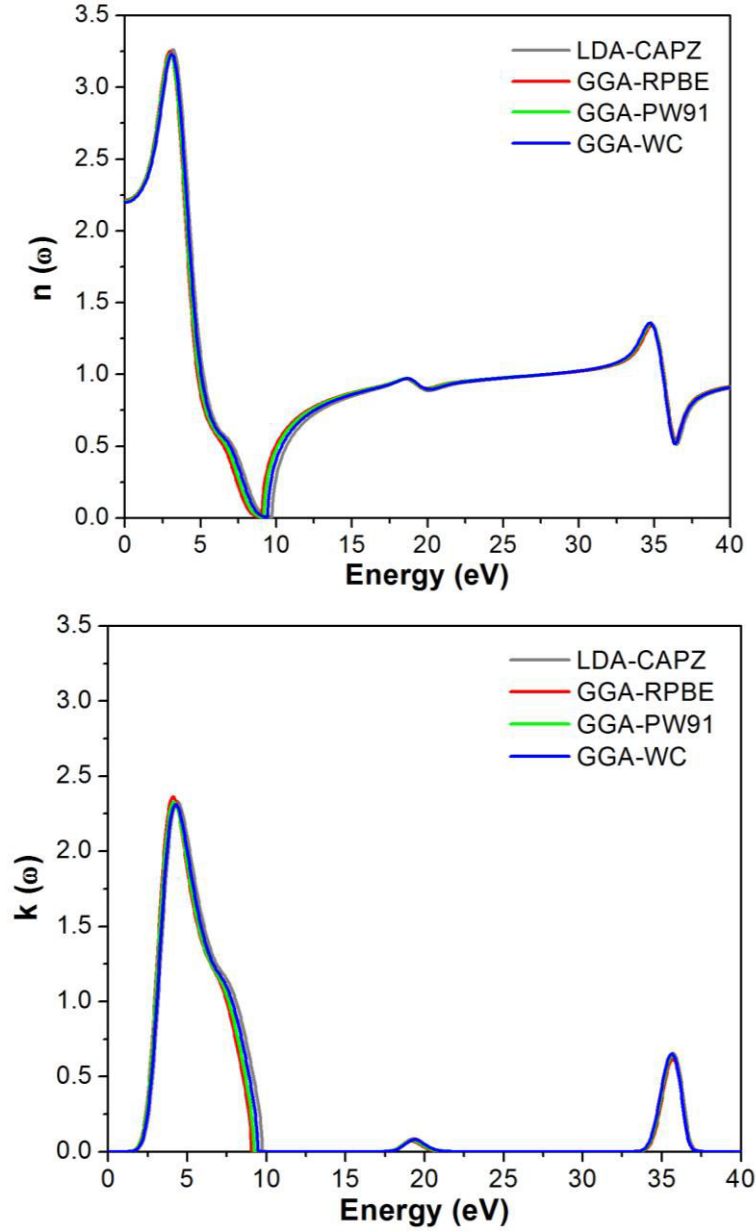


Figure 4: Refractive index and extinction coefficient of brookite TiO_2

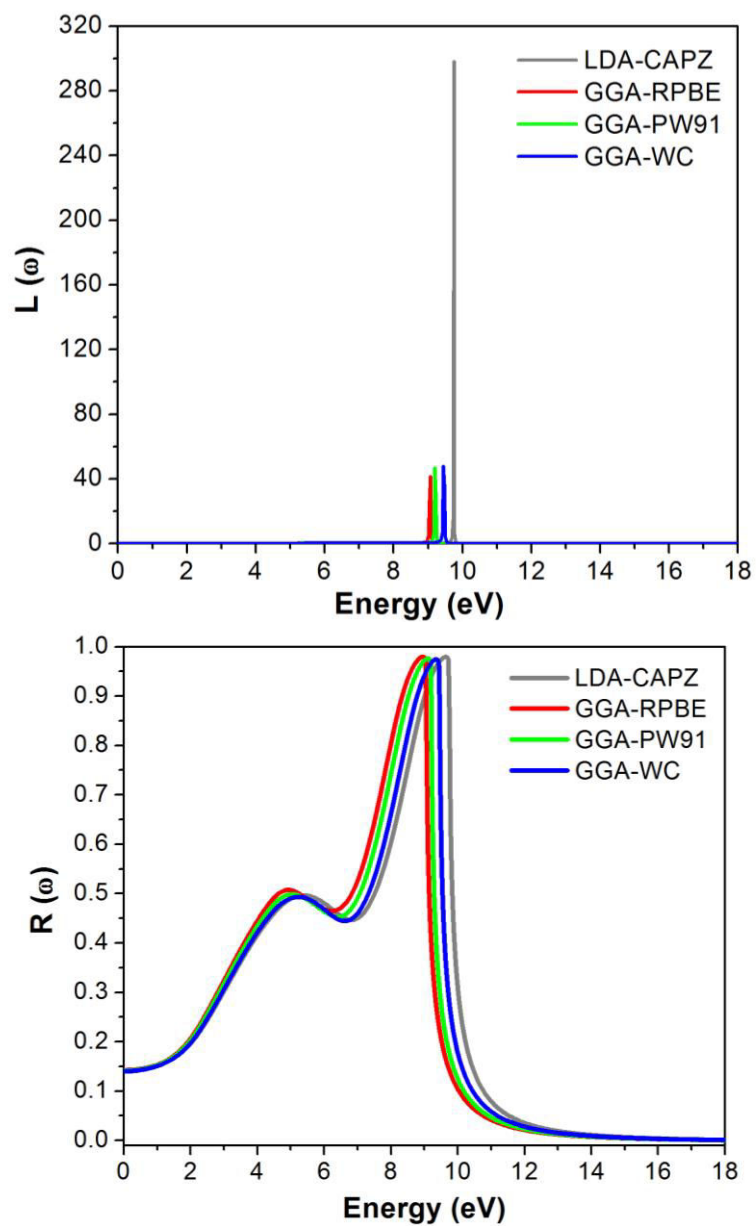
Other optical properties such as reflectivity, $R(\omega)$, energy loss function, $L(\omega)$ and absorption coefficient, $\alpha(\omega)$ are presented in Figure 5. These optical properties can be related with the dielectric function through the following relation:

$$R(\omega) = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (5)$$

$$L(\omega) = \text{Im}\left(\frac{-1}{\varepsilon(\omega)}\right) \\ = \frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} \quad (6)$$

$$\alpha(\omega) \\ = \frac{2k\omega}{c} \quad (7)$$

The loss function $L(\omega)$ is energy loss of electron when passing through uniform dielectric materials. The major peaks of energy loss for brookite TiO_2 is positioned in the range of 9.02 to 9.82 eV within 18 eV of photon energy. The energy peaks of loss function are match to the sharp decline in the reflection spectra. The major peak of reflection spectra from reflectivity $R(\omega)$ occurs in same energy limits as absorption spectrum. Besides, the major peaks of reflection spectra can be seen to occur where the peaks of dielectric function and refractive index start decreasing and become zero. The absorption coefficient $\alpha(\omega)$ determines how far light of a particular wavelength can penetrate into a material before it is absorbed. The energy and wavelength of absorption is defined by the difference between energy levels of an electronic transition. The corresponding peaks in the absorption spectrum are located within the ranges 2.11 to 9.77 eV. The optical absorption of brookite can be observed to occur in ultraviolet light region at an absorption edge from 300 to 500 nm.



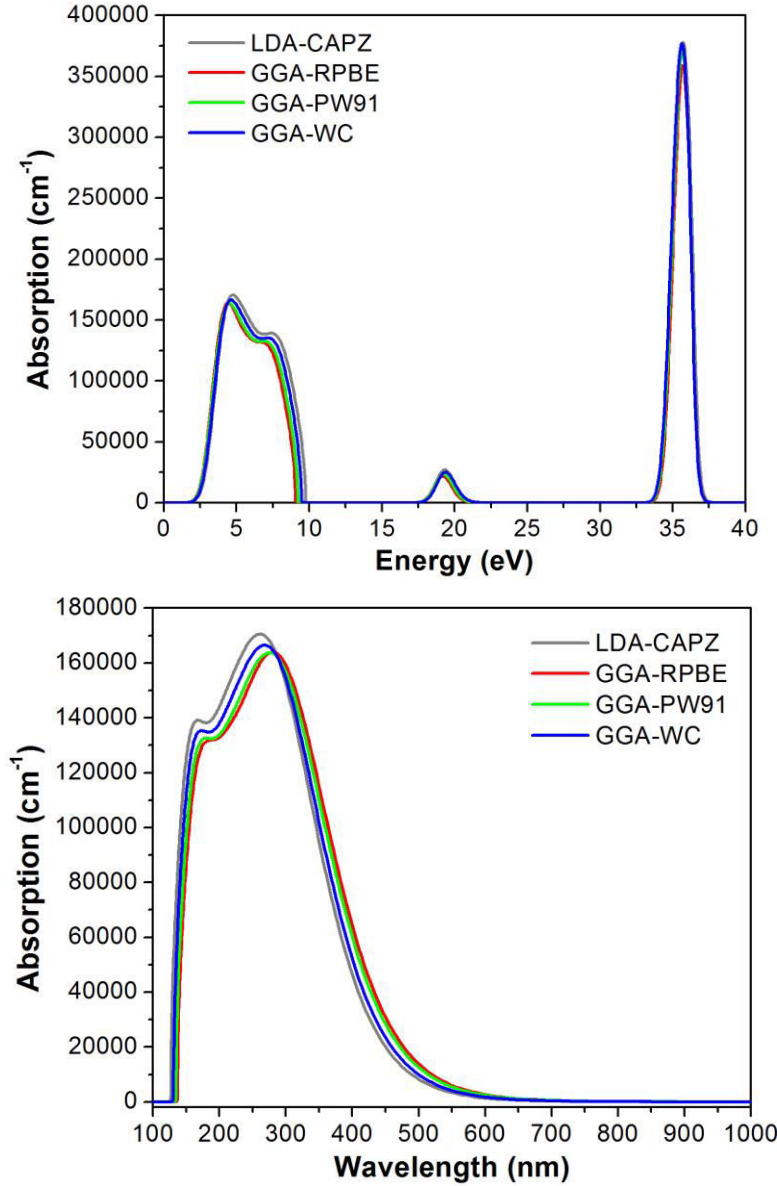


Figure 5: Reflectivity, loss function and absorption coefficient of brookite TiO₂

CONCLUSION

In conclusion, the first-principles calculations present the description of the structural, electronic and optical properties in the brookite TiO₂. The calculated structural parameter in GGA-WC is in better agreement with experimental values compared with LDA, GGA-RPBE and GGA-PW91. Brookite TiO₂ has a direct band gap of about ~2.3-2.5 eV calculated from LDA and GGA functional. Both the valence band and conduction band contain the contributions from O 2*p* and Ti 3*d*, indicating hybridization between these states. Optical calculations for dielectric constant,

refractive index, loss function and reflectivity are in good agreement with experiment. The optical absorption of brookite is found to be in the range of ultraviolet light region.

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