Comparative study of structural and electronic properties of TiO_2 at GGA and GGA+U level

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Besides the structural properties, electronic bandstructure investigations of two technologically important phases (anatase and rutile) of titanium dioxide (TiO_2) are studied in this research using DFT based first-principles plane-wave ultrsoft pseudo-potential (PW-PP) scheme of calculations as implemented in CASTEP computational code. In these Computations, for exchange-correlation functional, Perdew-Burke-Ernzerhof (PBE) parameterized generalized gradient approximation (GGA) and GGA+U are implemented, where 'U' is Hubbard correction parameter for screening self interaction. Optimum value of U applied in this study for rutile is 7.5eV, and for anatase is 9.0eV. Our calculated values of bandgap energy with PBE-GGA for anatase and rutile structure are 2.140eV and 1.973eV respectively which are sufficiently underestimated in comparison with experimental measurements whereas computed bandgap energy values within the implementation of GGA+U are found to be 3.350eV and 2.557eV respectively. These results are in nice agreement to experiment. Furthermore, to obtain the equilibrium volume, bulk modulus and pressure derivative, equation of state calculations were taken into account. Our calculated results for structural properties for anatase (V_0=141.7 $\overset{0}{A}{}^3$, B_0=417.4GPa and B_0' =3.97, and rutile (V_0=65.68 $\overset{0}{A}{}^3$, B_0=153.24GPa and B_0' =3.7) phases agree well with experimental as well as previously reported first principles studies.

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1. Introduction

Metal oxides are investigated significantly due to their new generation technological applications. Among these, titanium dioxide (TiO_2) is catching more and more attention of researchers, and is studied broadly [1] due to its large scale industrial applications as a photo-catalysis, white pigments, gas sensor devices, heterogeneous catalysis, for water & air purification [2], novel bio-materials, light emitting diodes and coating materials, etc.

New optoelectronic applications of TiO_2 such as transparent conducting material in solar cell technology, has increased interest of material scientists manifold in the investigation of electronic structure and corresponding properties to exploit its potential for further applications in various devices. It is because, fundamental knowledge of physical properties is crucial for device applications, for example, in optoelectronic applications, the knowledge of electronic bandstructure is prerequisite to attain better efficiency and applicability [3].

In literature, different polymorphs of TiO_2 have been reported. Technological important anatase and rutile TiO_2 has been reported as a wide bandgap semiconductors, with bandgap energy of anatase phase 3.2eV [4] and of rutile 3.0eV [5], similar to other wide bandgap semiconductors, for example III-nitrides, zinc oxide [6-7] and diamond [8]. Wide bandgap nature of TiO_2 is also one of the features in attracting a great deal of the attention of researchers. Though number of studies have been carried out to investigate different physical properties within different computational approaches including FP-LAPW (full-potential linearized augmented plane-wave), OLCAO (orthogonalized linear-combination of atomic-orbitals), and Pseudopotential Hartree-Fock (PHF) [9-15], most of these studies report controversial and underestimated results within simple LDA and GGA in particular for systems having localized d or f electrons. It is because of the inappropriate depiction of the bandstructure due to the presence of intrinsic drawbacks of self interaction in standards LDA and GGA exchange correlation functional. This problem has been well tackled within DFT+U approach developed in 1990 [16-17] by taking into account overestimation problem of electron delocalization in standard DFT and treating electronic correlation through Hubbard like model for localized states. U parameter is used for this purpose.

Transition metal oxides are extensively investigated using DFT+U methods from last few years after the successful study of different oxides (MnO, FeO, CoO and NiO) [17-18] having localized d and f electronic states. Although appreciable improvement in the results of energetic, electronic and magnetic properties of insulators, within DFT+U, containing 3d transitions metals have been reported in a number of studies including the recent study related to phase stability of TiO_2 [19-23], a study with DFT+U of TiO_2 is necessitated to reveal precisely electronic bandstructure and electronic bandgap energy and other related properties.

In this paper, we extend and complete our very briefly presented work in a conference found at http://ieeexplore.ieee.org/xpl/login.jsp?tp=&arnumber=6149648, related to first principles study of the bandstructure of anatase and rutile TiO_2 besides the structural parameters using PBE-GGA [24] for the purpose of exchange-correlation functional as well as GGA+U [25-26]. The “U term” (Hubbard U) is a parameter which allows correlation effects to be included in density functional calculations. In perusing our work, we first optimized geometry of both polymorphs of TiO_2. In the next step, equilibrium structural parameters were obtained from optimized structure using equation of state. At the end electronic bandstructure was investigated using PBE-GGA together with GGA+U by using CASTEP computer code [27]. Computed results have been compared with earlier theoretical and experimental data. Our presented results by GGA+U exhibit considerable improvement over the preceding theoretical results and found to be consistent with experiment.

2. Computational method

Crystal structure of TiO_2 (anatase and rutile) was simulated using experimental lattice parameters and integrating related symmetry operation, space group, etc., from CASTEP database. The anatase TiO_2 belongs to the tetragonal crystal system; I41/amd space group (number 141). Similarly, TiO_2-Rutile also belongs to crystal system; P42/mnm space group (number 136). Electronic configuration of TiO_2 is Ti: $3s^2 3p^6 3d^2 4s^2$ and O: $2s^2 2p^4$. In our first principles study, inner-shell electrons (core electrons) of Ti ($1s^2 2s^2 2p^6$) and O ($1s^2$) are distinguished from valence electrons of Ti ($3s^2 3p^6 3d^2 4s^2$) and O ($2s^2 2p^4$).

Computations were performed in two steps; first the geometry optimization was performed for both anatase and rutile TiO_2 and then bandstructure was investigated from the optimized structure of anatase and rutile TiO_2. Calculations were executed in reciprocal k-space. To construct pseudopotential, “Ultrasoft pseudopotential” (USP) was used. The plane-wave cutoff energy was set as 300eV, and the convergence value of self-consistence field was ensured upto 2.0×10^{-6} eV/atom, while *k* point’s mesh of 3x3x1 for anatase and 4x4x4 for rutile TiO_2 under the Monkhorst-Pack scheme [28] were used. For exchange correlation energy functional and corresponding potential PBE-GGA and GGA+U has been used. In our work, computations with GGA+U were performed by allowing U to vary from 0 to 8.0 eV for rutile-TiO_2 and from 0 to 9.5 eV for anatase-TiO2. By comparing the results for different U values, optimum values of U=7.5eV for rutile and 9.0eV for anatase TiO_2 were obtained as shown in Fig. 1.

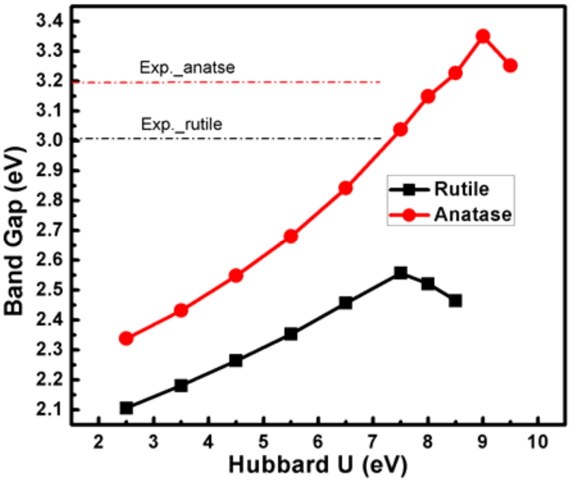

Fig. 1. Relation ship between rutile and anatase TiO_2 versus Hubbard U parameter.

3. Results and discussion

Structural properties: For anatase TiO_2, we used the values of lattice parameters as a=b=3.776 Å, c=9.486 Å. Similarly, for rutile TiO_2 we used a=b=4.594 Å and c=2.958 Å. The value of internal parameter ‘u’ is used 0.208 and 0.305 for anatase and rutile TiO_2 respectively. By using above mentioned lattice parameters, structure is simulated and then geometry optimization is performed by applying the Broyden- Fletcher-Goldfarb-Shenno (BFGS) [29] approach for both anatase and rutile TiO_2. Corresponding equilibrium values of structural parameters (volume, lattice constants, bulk modulus and its pressure derivative) are obtained by fitting data into equation of state. Obtained values of lattice constants (a=b=3.799 Å and c=9.814 Å) for anatase polymorph are minutely (~0.01%) higher than reported experimental results [30-31] but well consistent with earlier reported first principles theoretical results [13, 32-34]. Similarly, obtained values of lattice constants for rutile polymorph are, a=b=4.695 Å and c=2.965 Å that are also little (0.01%) higher than experiments [35-36] and comparable with previous theoretical results [32-34]. From Table 1, it can also be seen that the equilibrium volume (V_0=141.7 $\overset{0}{A}{}^{3}$) and bulk modulus (B_0=216.4 GPa) for anatase TiO_2 are 3.96 % and 37.6 % higher than experimental results respectively [31] but are in good agreement with other computational results [13, 33-34]. For rutile TiO_2, the obtained results of equilibrium volume (V_0=65.36 $\overset{0}{A}{}^{3}$) and bulk modulus (B_0=246 GPa) are 4.6 % and 16.04 % higher respectively as compared to experimental reported values [35-36] and consistent with former first principles calculations [33-34, 37]. Furthermore, we have calculated the pressure derivative of bulk modulus for anatase (B_0'=4.3) and rutile TiO_2 (B_0'=4.8) respectively. Our computed pressure derivative value of bulk modulus (B_0') for both anatase and rutile are 4.5 % and 23.8 % lower than experiment (4.5 and 6.3) respectively [31, 36]. Overall our computed results with PBE-GGA are in good agreement with previously reported results and consistent with experimental measurements. Comparison of calculated values of structural parameters of anatase and rutile TiO_2 with experimental [30-31, 35-36] and theoretical [13, 32-34, 37-38] results are presented in Table 1.

Table 1. Comparison between computational and experimental results of investigated structural parameters for anatase and rutile TiO_2.

		Structural parameters			**EOS parameters**		
Polymorph	**Method**	**a= b** ($\mathring{A}$)	**c** ($\mathring{A}$)	**u**	**V_0** ($\mathring{A}^3$)	**B_0** (GPa)	**B_0'**
Anatase	Our Present work **PBE-GGA**	3.799	9.814	0.206	141.7	216.4	4.3
	Exp. [30]	3.782	9.502	0.208	---	---	---
	Exp. [31]	3.785	9.512	----	136.3	179	4.5
	HF [13]	3.763	9.851	0.202	139.5	---	---
	GGA-PW91 [32]	3.8188	9.6875	0.2069	---	----	----
	PBE-GGA [33]	3.776	9.486	0.208	138.3	221	4.0
	LDA-PZ [34]	3.732	9.404	0.209	131	201	
	GGA-PW91 [34]	3.793	9.703	0.206	139.6	183	
	PBE-GGA [38]	3.885	9.690	0.208	---	----	----
Rutile	Our Present work **PBE-GGA**	4.695	2.965	0.308	65.36	246	4.8
	Exp. [35-36]	4.594	2.958	0.305	62.5	212	6.3
	GGA-PW91 [32]	4.6558	2.9674	0.3046	---		
	PBE-GGA [33]	4.594	2.959	0.305	63.3	235	4.0
	LDA-PZ [34]	4.535	2.909	0.303	59.8		
	GGA-PW91 [34]	4.637	2.960	0.305	63.4		
	LDA-VWN [37]	4.599	2.980	0.304	---	258	4.7

Electronic properties: By using the optimized values of lattice and internal parameters, Kohn Sham eigenvalue equations were computed in the brillouin zone along high symmetry directions, and the corresponding calculated bandgap energy values for both phases with PBE-GGA and GGA+U are presented in Table 2 together with reported theoretical [2, 10, 32, 38-44] and experimental [4, 39, 45-46] results. With PBE-GGA, obtained bandgap values 2.140 eV for anatase and 1.936 eV for rutile TiO_2, are 33.13% and 36.1% lower as compared with experimental values (3.2eV and 3.08eV) [4, 39] respectively. Although PBE-GGA produces reasonable results for structural properties, it underestimate the bandgap energy because of simpler form of functional used in this approximation which is not sufficiently flexible to give simultaneously both exchange correlation energy and its charge derivative accurately, and consequently results into overestimation of the electron delocalization: a well established problem of standard DFT methods specifically in systems containing localized d or f electrons.

To overcome this difficulty, exchange correlation functional GGA+U has also been used. The calculated bandgap energy values for anatase 3.35eV and for rutile TiO_2 2.557eV within GGA+U give sufficiently improvement over the simple GGA calculations as can be seen from Table 2 and closer to the experimental measurements as compared to GGA calculations [4, 39, 45-46].

Table 2. Comparison of computational and experimental results of bandgap energy for anatase and rutile TiO_2.

Name of polymorph	**Method/Ref**	**Exchange correlation (XC)**	**Band gap energy E_g (eV)**
Anatase			
Our present work	PP-PW	PBE-GGA	2.140 (Indirect)
	PP-PW	GGA+U	3.350 (Indirect)
Exp.	[4]	--------	3.20
Other calc.	FC-PAW [2]	LDA	1.874
	FP-PW [10]	LDA	2.13
	PAW **[**32**]**	GGA-PW(91)	1.88
	CASTEP [38]	PBE-GGA	1.803
Rutile			
Our present work	PP-PW	PBE-GGA	1.963(Direct)
	PP-PW	GGA+U	2.557(Direct)
Exp.	[39]	----------	3.08
	[45]		3.03
	[46]		3.031
Other results	FP-PW [39]	LDA-DFT	1.80
	PP-PW [32]	GGA-PW(91)	1.64
	PP-PAW [40]	LDA-DFT	1.70
	PP [41]	GGA-DFT	1.85
	PBE-PW [42]	LSD-GGA+U	2.00
	PP-PW [43]	PBE-GGA	1.87
	PP-PW [44]	PBE-WC-GGA	2.03

From the analysis of the anatase TiO_2 bandstructure, we observe indirect nature of bandgap between conduction and valence bands with PBE-GGA and GGA+U as can be seen from the Fig. 2 because maximum of valence band and minimum of conduction are lying at different symmetry points. Though we observe indirect nature of bandgap with PBE-GGA and GGA+U between conduction and valence bands, it can be seen from Fig 2 (a, b) clearly that the maximum of valance band with both forms of exchange correlation functional is lying at the same point right to the M-point but minimum of the conduction band with PBE-GGA is at G-point whereas minimum of the conduction band with GGA+U is slightly next to G symmetry point. This leads to indirect nature of bandgap with PBE-GGA from **M-G** and with GGA+U from **M-Z** whereas in a most recent study [23], direct nature (Γ- Γ) of anatase TiO_2 bandgap has been reported by taking into account U=2.5eV. It is well known fact that the standards LDA and GGA though underestimate bandgap value to experimental measurements but generally reveal similar nature of bandgap structure in comparison with experiment. It means our reported indirect nature of bandgap for anatase phase is more realistic than that of the recently reported work [23]. This observed anomaly in ref. 23 may be due to use of improper value of U parameters. This indicates bandstructure dependence upon the value of U parameter. The value of our reported bandgap energy 2.140eV (Fig.2 (a)) with PBE-GGA is much lower than the GGA+U i.e. 3.350eV (Fig.2 (b)) indicating that the role of exchange correlation dominantly affects the bandgap energy. It can easily be observed from the tabulated data in Table 2.

It may further be noted (Table 2) that our bandgap investigated results with GGA+U (U=9.0 are more realistic for anatase structure of TiO_2, and are closer to the experimentally reported value 3.2eV [4].

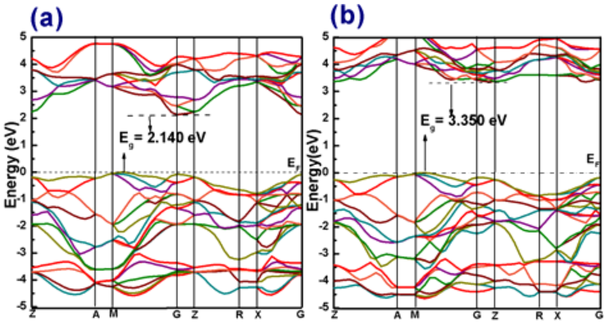

Fig. 2. Band structures calculated with PBE-GGA (a) and GGA+U (b) term for anatase TiO_2. The dashed horizontal lines show the Fermi energy, which is set as zero (eV).

In case of rutile TiO_2, we note that (Fig. 3) our calculated bandstructure with PBE-GGA and GGA+U are similar and direct bandgap nature at G-point except the difference in the numeral value of bandgap energy. It can also be seen from Table 2 and Fig. 3 that the calculated value of bandgap energy with PBE-GGA (1.963eV) lower as compared to GGA+U i.e. 2.557eV. Our computed value of bandgap energy with GGA+U for rutile structure is somehow lower than experimental results though, these values show appreciable improvement over simple PBE-GGA in comparison to the experimental measurements [39, 45-46] for rutile TiO2. Similarly our results with PBE-GGA are in agreement with preceding theoretical work [32, 39-44]. Table 2 also depicts that our results for bandgap energy with GGA+U are better than earlier theoretical work due to consideration of Coulomb interaction among the *d* electrons through Hubbard like model correction parameter U.

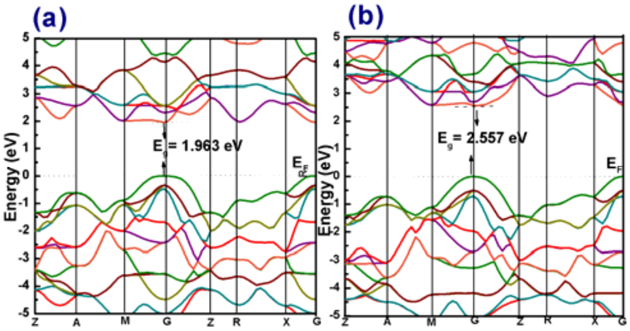

Fig. 3. Band structures calculated with PBE-GGA (a) and GGA+U (b) term for rutile TiO_2. The dashed horizontal lines show the Fermi energy, which is set as zero (eV).

Some important features of this study are summarized as follows:

1. This is our first comparative reported study of electronic bandstructure properties for TiO_2 (anatase and rutile) in the literature using PBE-GGA together GGA+U by state of the art CASTEP computer code based on DFT.
2. Our calculated structural parameters (lattice constants, equilibrium V_0, B_0, $\mathbf{B}_0'$) for anatase and rutile TiO_2 are in good agreement with experiment [30-31, 35-36] and have significant improvement over previous theoretical results [13, 32-34, 37-38].
3. The pressure derivative of bulk modulus is obtained by using the third order Birch Murnaghan equation of state [47] and the obtained values for anatase and rutile are in consistent with experiment [31, 36] and have significant improvement over other theoretical results [13, 37] respectively.
4. It may be observed that obtained bandgap energy values for both polymorphs with PBE-GGA and GGA+U show a noteworthy improvement over other computational DFT based approaches.
5. Our PBE-GGA and GGA+U calculations regarding anatase TiO_2 exhibit indirect nature of bandgap which is not favoring to the direct nature of bandgap as reported in ref. 23. This contradiction may be due to use of inappropriate value of U parameters in their calculations.
6. It is also observed that PBE-GGA for both polymorphs of TiO_2 gives much lower values of bandgap energy whereas GGA+U produce reasonable results because of taking into account effect of self interaction.

4. Conclusion

DFT based first principles calculations on anatase and rutile TiO_2, using ultra-soft pseudo-potential approach as incorporated in CASTEP computer code, have been performed. Our calculated electronic bandstructure results with GGA+U are in good agreement to reported experimental work and show improvement over earlier computations with LDA and GGA work. GGA+U was found a suitable approach to get better exchange correlation potential for bandstructure calculations related to the materials having localized d or f electronic states. It was also observed that accuracy of DFT+U calculations are very sensitive to U parameter. A special care should be taken to obtain optimum value of U to reproduce reliable bandstructure results. Besides electronic properties, our obtained values of lattice constants (a=b, and c), internal parameter (u), equilibrium volume (V_0), bulk modulus (B_0) and pressure derivative of bulk modulus (B_0') for anatase and rutile TiO_2 agrees nicely with experiment and exhibit considerable improvement over earlier reported computational studies.

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