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Study of Structural and Electronic Properties of Rutile Titanium Dioxide (TiO_2) Using Density Functional Theory (DFT)

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ABSTRACT

The study aims to investgate the structural and electronic properties of Rutile TiO_2 due to its wide range of applications, and is a promising material for the mass market for low-cost, high-efficiency and optic-electronic devices because of its outstanding properties, inherent n-type conductivity, low toxicity, and availability[1]. All these modern applications call for better understanding of its properties, but there is a lake of investgation on the structural, elacronic and elastic properties of R-TiO_2 using LDA exchange-correlation function[2]. In this project, band structure, the density of state, and structural optimizations of rutile titanium dioxide were studied and analysed using the Quantum-Esprssso package and LDA exchange-correlation function[3], [4]. By performing this calculation, the estimated lattice parameter 'a' for rutile titanium dioxide using LDA method is 4.5653Å and 'c' is 3.1422 Å, which are relatively close to experimental results which are 4.593 Å and 2.9 Å. Also, According to the results, rutile titanium dixoide(R-TiO_2) has a direct band gap semiconducting property with an energy gap of 1.50eV using LDA exchange correlation function.

Keywords- Rutile titanium dioxide, LDA exchange-correlation function, Density functional theory (DFT).

I. INTRODUCTION

Recently the Titanium dioxide has been the subject of theoretical and experimental studies from decades, because of its unique properties[5],[6]. It has good photocatalytic activity and a high dielectric constant with a wide range of electrical conductivity[7]. Here are three common polymorphs of TiO_2 namely; (i) rutile phase with a tetragonal, space group of P42/mnm and Eg ~ 3.05 eV, (ii) anatase phase with a tetragonal space group of I41/amd and Eg ~ 3.23 eV and (iii) brookite phase with a band gape of Eg ~ 3.26 eV)[9].

Crystal parameters are a = 4.594 Å, c = 2.959 Å for rutile, a = 3.785 Å, c = 9.514 Å for anatase and a = 5.456 Å, b = 9.182 Å, c = 5.143 Å for brookite[10]. Between all these three polymorphs of TiO_2, the rutile is the most stable phase of TiO2 and has a wide range of application due its uniqe properties, such as high refrective index, stabilility at a high tempereture[11]. Also, the rutile phase have gotten more attention than the anatase and brookite due its key characteristics, including the optical property and electrical bandgap[12]. The Brookite and Anatase phases have been extensively studied compared to the Rutile phase. This may be because it is computationally expensive due to the number of atoms in its unit cell and its difficulty in preparation[10]. Some of its important properties, for instance the structural and electronic properties are still under deliberation. As a result, more investigation into rutile phase properties is needed to understand its potential uses better. Following this introductory we describe computational approach and the DFT method.We present and discuss electronic energies and related properties of rutile TiO_2, as obtained by our self-consistent solution of the relevant system of equations defining the local density approximation (LDA). We compare our findings to previous, corresponding theoretical and experimental ones. Finally, we summarize our results.

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II. METHODOLOGY

The Quantum Espresso algorithm was used to do the structural optimization and electronic calculation utilizing the density functional theory-supported plane wave pseudopotential approach[13]. Pseudopotential (PP) is utilized to model the electron-ion interaction while the electron-electron interaction is modeled with the help of the local density approxmation (LDA)[14]. For the exchange-correlation interaction, LDA method has been employed.This exchange-correlations was chosen because no adjustable parameter was required hence computationally efficient. Plane wave method was used to represent electronic wave function. Crystal structures were relaxed at T=0K and P=0 GPa and convergence tests were carried out. After doing convergance tests, the cutoff energy of 200 eV was selected.

Then, all of the provided computations are done utilizing this optimized structure. In addition, all the calculations were done using Quantum Espresso pakge. First of all, structural optimization was run with x driver and self consistent calculation was run with scf driver to get the electron denstiy. Also, the band sructure calcualtion was run with $bands.x$. In order to generate more datae the post processing tool was run with $pp.x$ driver. In addition, by using the Quantum Espresso pakge the parameters, such as; the Brillion zone grid, crystal systems, the kinetic cut-off energy, and the lattice, was quantified in an input file, with kinetic energy cut-off as well as different convergence thresholds for the selfconsistent field used till suitable values are obtained. Lattice parameters of R-TiO2 were obtained in two steps. In the first step, the convergence calculations of the total energy were performed using different kpoints generated with the method of Monkhorst and Pack[15]. The MonkhorstPack grid is a standard technique for collecting samples from the Brillouin zone (Monkhorst and pak 1976)[16]. The accuracy of the convergence is totally reliant on the integration grid selected. The Monk horst-Pack approach provides for both accurate integration of parts in the Brillouin zone, as well as sampling on the whole Brillouin zone[17]. Different k-point samplings were used for convergence test for the unit cell. Energy difference for the unit cell change was less than 0.0001 eV when the k-point grid was 12×12×3. This energy did not change further when I increased the k-point grid. This procedure was used for LDA method. In the second step, we tested the evolution of the total energy as a function of the lattice constant for R-TiO_2. Similarly, to get optimum value for cut-off enegy, the cut-off energy was ranged from 50 eV to 200 eV. The energy was converged at cut-off 200 Ry, so all the caculations were done by applying this optimized value (200 Ry) for cutoff energy. During the process of optimizing the lattice parameters, experimental lattice parameter values were taken into account as the starting point[18]. The Birch-Murnaghan equation of state was used to fit the data, and the lowest value of the fitted curve was used to determine the required lattice constant[12]. To get the highest possible value for the plane wave cut-off energies, the cut-off energy was increased from 50 Ry to 200 Ry after checking that the lattice parameters plus k-point meshes were created to their ideal values. When there was no longer any area for the energy to be changed, the perfect values were found. Given that every system aims to be in a low-energy state, this was a very important point (ground state). In addition, the Xcrysden tool was used to visualize the crystal structures of R-TiO_2. Also, for band structure calculation the k-points grid is most improtant parapmeter for LDA method[19]. In this particular piece of work, the building of the specific k-points was achieved by the use of the Monkhorst-Pack approach[20]. When calculating the band structures of the systems, Kokalj and Causà found that it was necessary to take into account the points and pathways with a high degree of symmetry that were created by the Xcrysden software[21]. In order to get more insight of band structure the total density of state (TDOS) and portail density of state (PDOS) using LDA XC functional was plotted using origine tool.

III. RESULT AND DISCUSSION

3.1 Structural Optimization

Geometrical relaxation is the first stage in any first-principles calculation to eliminate a certain amount of uncertainty to accurately forecast other values such as the electronic bandgap and elastic characteristics. Geometry optimization is a computational procedure in which atomic coordinates and cell parameters are modified so that the structure's total energy is minimized and a stable system is obtained[24]. A stable geometry will result from all optimization techniques. When the atoms in each optimal geometrical structure are relaxed and possibly stable, they will feel no forces or stress. As a result, full geometry optimizations of TiO_2 structures were carried out. Tetragonal rutile TiO_2 with lattice parameters a=b≠ c, α=β=γ=90o is the system being studied[25].

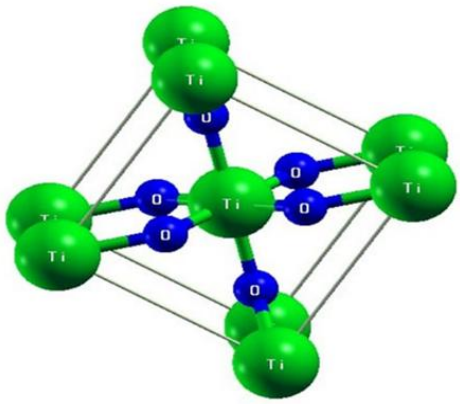

Figure 1: Optimized structures for rutile TiO_2.

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Table 1 shows the TiO_2 lattice constants from the DFT-LDA and the related experimental results. To avoid specific errors and obtain correct results for structural and electronic properties, the optimized lattice parameters of a and c, as shown in table (1), are used for this calculation.

Table 1: Calculated Lattice Parameters of R-TiO_2

Bulk TiO_2	XC	a (Å)	c (Å)	Ref.
R-TiO_2	LDA	4.653	3.1422	Present work
R-TiO_2	Experiment	4.5938	2.9586	[26]

The computed lattice parameter 'a' for TiO_2 using LDA-PZ is 'a' 4.653 and 'c' 3.1422, whereas the published experimental value for TiO_2 is 4.5938 and 2.9586[26] , [27]. Consequently, it was established that LDA-PZ represents the materials' features more accurately. According to the findings of this comparative study, the choice of XC functional has a significant influence on the ground-state properties of materials. The determined bond angles for TiO_2 using LDA-PZ are 131.94º and 90.00º, which are on average identical to the experimental and other LDA functional values from table 2. In general, it was discovered that, while LDA functional is inadequate at expressing the electrical characteristics of these confined orbitals, it does a great job of characterizing the energy of the system and accurately replicating the structural features[28]. By relaxing the TiO_2 structure's atomic locations and lattice characteristics, ground state simulations were conducted, and then lattice parameters were then compared to experimental results.

Table 2: Bond Angles and Bond Lengths for R-TiO_2

	R-TiO_2 (Bond lengths Aº)		R-TiO_2 (Bond angles Aº)	
Present work (DFT)	Ti –O	1.96	Ti-O-TiO-Ti-O	**131.94º 90.00º**
DFT [29]	Ti –O	1.85	Ti–O-TiO-Ti-O	**131.92º 90.00º**
Experiment work [30]	**Ti –O**	**1.95**	**Ti–O-Ti O-Ti-O**	**130.97º 90.00º**

3.2 Electronic properties

It is generally acknowledged that DOS and electronic band structure play key roles in establishing crystal structure[26]. Fundamentally, the categorization of materials, especially metals, semiconductors, and insulators, depends on a system's electronic characteristics. The size and presence f the energy band gap between the conduction band and the valence band determine the kind of material.

The electronic are Fig. 2 illustrate the electrical band structures of bulk TiO_2 estimated using LDA exchange correlations and pseudopotential. Regardless of whether exchange correlations or pseudopotentials are utilized, the computed band gap is underestimated compared to the experimental value. TiO_2's empirically observed bandgap is 3.0 eV; our computational estimates show band gaps ranging from 1.54 eV to 2.53 eV. The band gap using LDA exchange correlation is 1.54. The conduction band minimum at -point and the conduction band minimum at R and M are almost equal, according to our estimates of the electronic band structure. This degeneration is present in all exchange correlations and pseudopotentials[29]. We concluded that various bulk TiO_2 band configurations did not predict the band gap nor the norm-conserving pseudopotential.

Table 3: Calculated Energy Band Gap of TiO_2

compound	XC	Bandgap (eV)	Ref
R-TiO_2	LDA	1.54	Present work
R-TiO_2	LDA	1.5	[2]
R-TiO_2	Experiment work	3.03	[30]

In addition, for TiO_2, our calculation result is 1.54 eV for direct band gap using LDA which is pretty close to other LDA values, certifying the reliability of our methods. As a result the obtained result shows that, the LDA exchange-correlation is a good method for determining TiO_2's band structure. The Projected density of states (PDOS) is depicted in Fig. 2 using LDA. In the DOS analysis method, we set the Femi levels to 0 eV to enable comparability[30]. Based on our calculations, we also found nonzero Ti-PDOS in the valance band and nonzero O-PDOS in the conduction band close to the Fermi level. These nonzero PDOS values imply a substantial hybridization between Ti atoms' 3d orbitals and O atoms' 2p orbitals. In addition, we discovered two

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different peaks in the PDOS of the Ti3d orbital, showing a clear split into sub-bands. The sub-band separation of the 3d orbital of Ti atoms is discussed in the crystal-field theory of transition-metal (di) oxide complexes. Such d-states are divided by crystal field theory into three-fold degenerate t2g-like dxy, dyz, and dxz type states and two fold-degenerate eg-like states with and character. Furthermore, for the range of R-TiO_2 from -6 to -0.55, the density of state of R-TiO_2 is classified into three groups of occupied and unoccupied states, separated by gaps, using LDA exchange-correlation.

The O 2p and Ti 3d of O and Ti atoms contribute the most to the R-TiO_2 from -6 to –0.55. Second, no states exist between 0.55 and 0.93. Finally, O 2p and Ti 3d states contribute to total DOS from an energy range of 0.966 to 2.988 eV. Our analyses indicated that the best strategy to explain the electrical structure of TiO_2 other functional materials is to use a mix of LDAand pseudopotential [26].

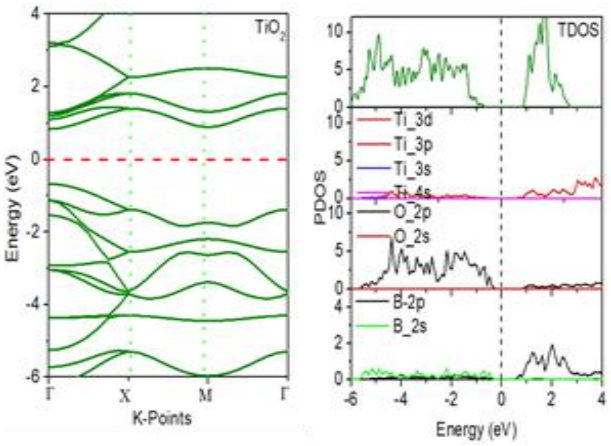

Figure 2: Electronic Band Structures and T-DOS of TiO_2, Using LDA Exchange-correlation

IV. CONCLUSION

This paper presents the findings of first-principles analyses of the structural, electrical, and elastic characteristics of TiO_2's Rutile phase. The Quantum Espresso algorithm was used to do the structural optimization and electronic calculation utilizing the density functional theory-supported plane wave pseudopotential approach**.** The estimated lattice parameter 'a' for rutile titanium dioxide using LDA method is 4.5653Å and 'c' is 3.1422 Å, which are relatively close to experimental results which are 4.593 Å and 2.9 Å. The Rutile structure was discovered to have a small band gap of 1.54 eV using the LDA exchange-correlation function which is in good accord with the experimental values and previous LDA based calculations.This shows significant improvement compared to other theoretical calculations[2]. The k-points of 12×12×3 were used for band structure calculation.

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