Comparative study on structural, electronic, optical and mechanical properties of normal and high pressure phases titanium dioxide using DFT

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Abstract

In this paper, a Self-consistent Orthogonalized linear combination of atomic orbitals (OLCAO) technique with a generalized gradient approximation such as Perdew–Burke–Ernzerhof Solid (GGA-PBE SOL) has been used to scrutinize the structural, optical, electronic and mechanical properties of normal pressure phase (Anatase and Rutile) and high pressure phase i.e., cubic (Fluorite and Pyrite) TiO₂. Electronic and optical properties of normal pressure phases of TiO₂ are also investigated using (Meta) MGGA-Tran and Blaha (TB09) and obtained results are a close approximation of experimental data. It is seen that the virtually synthesized structural parameter for cubic and tetragonal phases of TiO₂ are consistent with experimental and theoretical data. From the effective mass of charge carriers (m*), it can be observed that pyrite TiO₂ is having lower effective mass than the fluorite and hence shows higher photocatalytic activity than fluorite. Furthermore, it is seen that fluorite is more dense than anatase, rutile and pyrite TiO₂. From the theoretical calculations on the optical properties, it can be concluded that optical absorption occurs in the near UV region for high and normal pressure phases of TiO₂. Again from the reflectivity characteristics R(ω), it can be concluded that TiO₂ can be used as a coating material. Elastic constants, elastic compliance constants, mechanical properties are obtained for anatase, rutile, fluorite and pyrite TiO₂. A comparison of the results with previously reported theoretical and experimental data shows that the calculated properties are in better agreement with the previously reported experimental and theoretical results.

1. Introduction

TiO₂ occurs in many different forms. The naturally occurring forms of TiO₂ are TiO₂-B(Bronze), brookite, anatase and rutile [1]. Other forms of TiO₂ are columbite [2], baddeleyite [3], cotunnite [4], pyrite, fluorite, Tridymite [5], hollandite [6] and bronze [7, 8]. TiO₂ is a promising candidate in applications such as, coatings solar cells, photocatalysis, white pigment, biogas sensors, energy storage, etc, [9–18]. Nanotubes [19], nanowire [20] made from TiO₂ with suitable doping, thin films [21] of rutile TiO₂ with PbO₂ coating are found to be suitable in Dye Sensitized Solar Cells (DSSC’S). Also, adsorption of hydroxamate onto anatase TiO₂ surfaces [22] increases electron transfer event with less time period. Hence, it is more appropriate for energy harvesting applications. Since last decade, high-pressure phase TiO₂ is gaining attention because of its unique properties which play an important role in various applications. Cubic TiO₂ is formed by heating anatase TiO₂ at a high temperature of about 1900–2100K under high pressure of about 48 GPa in a diamond anvil cell [23, 24]. Cubic TiO₂ is the best choice for solar photovoltaic applications to extract solar energy and a healthy choice for a hazard-free environment [25].
There exist several approaches to theoretically investigate the properties of this material such as local density approximation (LDA) and generalized gradient approximation (GGA), MGGA under the framework of DFT along with various exchange-correlation functional. Gong sai et al [26], used TB-mBJ (Tran-Blaha modified Becke-Johnson) potential and obtained properties were in better agreement with the experimental results and considered to be much better compared to LDA and GGA approach. Zhi-Gang Mei et al [27], used LDA and GGA along with various exchange correlations for calculating structural, mechanical and phonon properties of rutile and anatase TiO2 and found that GGA-PBES provide accurate structural and mechanical properties for both the phases. Samat et al [14], calculated structural, optical and electronic properties of brookite TiO2 using GGA with various exchange-correlation and found that structural properties calculated using GGA-WC are in good agreement with experimental values than the remaining exchange-correlation. Shatendra Sharma et al [28], calculated the electronic and optical properties for Strontium Sulphide (SrS) using LDA, GGA, and MGGA and observed that MGGA gives the bandgap value more close to experimental value while LDA and GGA gives underestimated results. Dash et al [25, 29], used OLCAO–LDA–Perdew and Zunger (PZ) (1981) method to investigate various properties of anatase and cubic TiO2 and found an improvement in mechanical properties. Coronado et al [30], also used OLCAO-GGA method to verify the experimental data with theoretical data.

Researchers have calculated the structural, elastic, electronic, optical, thermal and acoustic properties of various phases of TiO2 theoretically [6, 23, 25, 26, 29, 31–38] as well as experimentally [11, 30, 39–42]. Zhang et al [43], analyzed the photocatalytic activity among natural phases of TiO2 based on the comparison of effective masses for these polymorphs and found that anatase is having higher photocatalytic activity than other two polymorphs. Mattesini et al [44] and Mahmood et al [26], found that fluorite TiO2 is having a more absorptive transition in the visible region compared to pyrite TiO2. As fluorite and pyrite are having cubic symmetry, it has only one dielectric tensor whereas tetragonal phases are having two dielectric tensor [45].

From the literature, it reveals that all the properties of TiO2 are sensitive to exchange correlation used. OLCAO is able to give effective improvement in terms of different elastic and mechanical properties rather than plane wave and other theoretical results. GGA-PBESOL provides better structural and mechanical properties than other exchange correlations. Hence, the first objective of this work is to carry out detailed analysis of the structural, electronic, optical and mechanical properties of high pressure and normal pressure phases of TiO2 using OLCAO-GGA-PBES. Second objective is to provide a detailed comparison of the obtained results of high pressure and normal pressure phases of TiO2 with each other and with previously available experimental and theoretical data. However, GGA also causes overestimation of lattice constants and underestimated bandgap value. Third objective is to get results consistent with experimental data. As experimental data is available for normal pressure phases of TiO2, MGGA-TB09 [46] is used here for analyzing its electronic and optical properties. The last objective is to calculate the m* of charge carriers for the cubic phase of TiO2 to find its possible application in photo-catalytic activity and compared with other phases of TiO2.

The rest of the paper is arranged as follows. Section 2 explains the adopted computational details for the analysis of all properties of TiO2. Section 3 details the results and discussion on obtained properties. Finally, sections 4 and 5 gives the conclusion and future scope of the work.

2. Materials and methodology

Here, computations are carried out for anatase, rutile, fluorite and pyrite TiO2. Anatase and rutile belong to tetragonal crystal system whereas fluorite and pyrite belongs to cubic crystal system. Anatase [29], rutile [39] and fluorite [11] TiO2 structures are created using experimental lattice parameters and wyckoff positions whereas for pyrite the lattice constants considered are \( a = b = c = 4.844 \text{ Å} \) [25]. Structure has been optimized using maximized force of 0.005eV/Å and maximum step length of 0.5 Å. Zero constraints are considered during optimization. The Limited Memory Broyden-Fletcher-Goldfarb-Shanno (LBFGS) [47–50] is adopted for the optimization of all structures because of its effectiveness for estimation of parameter in machine learning. It is based on the approximate Hessian matrix. At every iteration, it updates the approximated Hessian matrix by using products of vector–vector. With minimum iterations, it obtains its local minimum without sticking at the time of calculation. Furthermore, energy minimization is also carried out by varying lattice constants for all the structure under consideration to obtain the characteristic plot for the total energy versus total volume, which are shown in figures 2(a) and (b) for high and normal pressure TiO2, respectively. The lowest energy lattice constants are considered for simulation because minimizing the total energy of the crystal determines an appropriate set of linear combination of coefficients. OLCAO method [51] is applied here in the framework of Density Functional Theory (DFT), which is an all-electron technique applied for calculating \( 3p^{6}4s^{2}3d^{2} \) and \( 2s^{2}2p^{4} \) states as valence electrons for Titanium and Oxygen atom respectively. The optimized lattice structures of fluorite, pyrite, anatase and rutile TiO2 are shown in figures 1(a), (b), (c) and (d), respectively. The prediction of the molecular orbitals by this method is accurate due to the orthogonal simulation pattern. The LCAO method initially assumes that the
total number of atomic orbitals is equal to the total number of molecular orbitals included in the linear expansion. We have used GGA with PBE SOL [52] as exchange-correlation functional. Also used MGGA-TBO₉ exchange-correlation functional to analyzed electronic and optical properties of normal pressure phases of TiO₂. Other parameters like van der Waals corrections, spin–orbit coupling and Hubbard U are disabled. The Density mesh cut off is taken as 140 Hartree for all the structures. Sampling is done using the Monkhorst–Pack scheme [53] and set at 6 × 6 × 7 for anatase and rutile, 12 × 12 × 12 for fluorite and 7 × 7 × 7 for pyrite. State of art norm-conserving pseudopotentials have been used [54] for both Titanium and oxygen atoms.

The biggest benefit of approximate Linear Combinations of Atomic Orbitals (LCAO) method is its correctness in observable properties of molecules over other methods. The approximations used in LCAO method are superior than that of self-consistency field calculations. In addition, the approximation used in LCAO method is beneficial because they provide a relation between an orbital description and chemical intuition. GGA-PBE is most widely used approximation. PBE is the improved to PBESOL by making changes in two parameters. PBESOL provides improvement in equilibrium properties of bulk. By restoring gradient expansion for exchange, PBESOL provide lattice parameters lower than PBE and cohesive energies with less accuracy. Electronic properties such as bandgap value using GGA are underestimated because a single exchange-correlation potential is not continuous across the gap. To enhance electronic properties MGGA family of functional extend the GGA approximation by additionally depending on the Laplacian of the density and kinetic energy density. Hence, MGGA gained substantial achievement in the improvement of electronic properties.

3. Results and discussion

3.1. Structural parameter

Structural optimization of anatase, rutile, fluorite and pyrite TiO₂ is carried out by varying lattice constant and finding out the lowest energy point. For simulation, a totally relaxed Wyckoff position and experimental cell volume [11, 29, 39] is considered. The lattice constant as obtained from the figures 2(a) and (b) are a = 4.804 Å for fluorite and a = 4.869 Å for pyrite and a = 3.796 Å, c = 9.617 Å for anatase and a = 4.616 Å, c = 2.961 Å, for rutile. Table 1 represents a comparison of the calculated density, structural parameters, volume and bandgap (Eg) with previously reported theoretical and experimental values.

3.2. Electronic properties

The energy band structure is an important property of any material which describes the optical and electronic properties. The energy bandgap is defined as the minimum energy required to create an electron and hole pair in the semiconductor. Whereas, the optical bandgap is the excitation energy which determines the onset of vertical interband transitions. Two properties namely, the band structure and total density of states are studied here and analyzed in detail. Figure 3(a) represents the band structure and 3 (b) represents the total density of states (TDOS) for fluorite TiO₂. From the band diagram of fluorite TiO₂, it can be observed that Fermi energy is more
closed to the conduction band whereas, the minima energy point of the conduction band and maxima energy point of valence band lie on the same line G, implying a direct bandgap having a value of 1.07 eV. It is seen that 14 bands are having a width equal to 7.34 eV below the Fermi level. These bands are the result of the mixing of atomic orbitals O 2p and Ti 3d. 10 bands are having a width 4.38 eV above the Fermi level. These bands are the effect of the Ti 3d orbitals contribution. It is observed from figure 3(b) that the highest points (peak) occur on the top of the valence and bottom of the conduction band at $-2.79 \text{ eV}$, $-1.81 \text{ eV}$ and $2.12 \text{ eV}$, $2.36 \text{ eV}$ due to mixing of atomic orbitals Ti 3d and O 2p respectively. Occupied states between oxygen 2p and titanium 3d which ranges

![Image](image-url)  
**Figure 2.** Total Energy versus volume of (a) High pressure phases of TiO$_2$ and (b) Normal pressure phases of TiO$_2$.

| Phase      | Method         | Density($\rho$)(gm cm$^{-3}$) | a(Å)  | c(Å)  | $V_0$(Å$^3$) | Bandgap (eV) | References |
|------------|----------------|-------------------------------|-------|-------|-------------|--------------|------------|
| Fluorite   | OLCAO-GGA PBESOL | 4.78                          | 4.804 | —     | 110.889     | 1.07(D)      | This Work  |
|            | GGA-PW91        | —                             | 4.828 | —     | 112.5       | 1.136(D)     | [23]       |
|            | GGA-WC          | —                             | 4.786 | —     | 110         | 1.123(D)     | [23]       |
|            | GGA-PBESOL      | —                             | 4.782 | —     | 109         | 1.120(D)     | [23]       |
|            | GGA-RPBE        | —                             | 4.865 | —     | 115         | 1.151(D)     | [23]       |
|            | GGA             | —                             | 4.829 | —     | —           | 1.154(ID)    | [6]        |
|            | OLCAO-PZ        | —                             | 4.787 | —     | 109.696     | 0.89(D)      | [25]       |
|            | GGA-PW91        | 4.749                         | 4.817 | —     | 111.77      | —            | [31]       |
|            | Experimental    | 4.59                          | 4.87  | —     | 115.50      | —            | [11]       |
| Pyrite     | OLCAO-GGA PBESOL | 4.59                          | 4.869 | —     | 115.43      | 1.369(ID)    | This Work  |
|            | GGA-PW91        | —                             | 4.891 | —     | 117         | 1.466(ID)    | [23]       |
|            | GGA-WC          | —                             | 4.851 | —     | 114.2       | 1.472(ID)    | [23]       |
|            | GGA-PBESOL      | —                             | 4.849 | —     | 114         | 1.474(ID)    | [23]       |
|            | GGA-RPBE        | —                             | 4.927 | —     | 119.6       | 1.457(ID)    | [23]       |
|            | GGA             | —                             | 4.8940| —     | —           | 1.457(ID)    | [6]        |
|            | OLCAO-PZ        | —                             | 4.844 | —     | 113.661     | 1.18(ID)     | [25]       |
|            | GGA-PW91        | 4.563                         | 4.881 | —     | 116.28      | —            | [31]       |
| Anatase    | OLCAO-GGA PBESOL | 3.825                         | 3.79685| 9.61702 | 69.3198     | 2(ID)        | This work  |
|            | MGGA-TBO9       | —                             | —     | —     | —           | 3.3(ID)      | This work  |
|            | GGA-PW91        | —                             | 3.784 | 9.712 | 69.539      | —            | [31]       |
|            | GGA-PBESOL      | 3.902                         | 3.7767 | 9.5349 | —           | —            | [33]       |
|            | DFT             | —                             | 3.8   | 9.7   | —           | 2.13(ID)     | [33]       |
|            | PBE-GGA         | —                             | 3.811 | 9.631 | 69.947      | 2.14(D)      | [36]       |
|            | WC-GGA          | —                             | 3.784 | 9.512 | 68.066      | —            | [36]       |
|            | OLCAO-PZ        | —                             | 3.7842| 9.5146 | —           | —            | [29]       |
|            | EXP             | —                             | 3.785 | 9.512 | —           | —            | [39],[30]  |
| Rutile     | OLCAO-GGA PBESOL | 4.201                         | 4.6164| 2.9611 | —           | 1.81         | This work  |
|            | MGGA-TBO9       | —                             | —     | —     | —           | 2.98         | This work  |
|            | GGA-PW91        | 4.184                         | 4.630 | 2.957 | 63.41       | —            | [31]       |
|            | GGA-PBESOL      | 4.27                          | 4.5949| 2.9433 | 62.1422     | —            | [35]       |
|            | DFT             | —                             | 4.643 | 2.965 | 63.918      | 1.86(D)      | [33]       |
|            | PBE-GGA         | —                             | 4.634 | 2.976 | 63.912      | 1.94(D)      | [36]       |
|            | WC-GGA          | —                             | 4.643 | 2.881 | 62.107      | —            | [36]       |
|            | EXP             | —                             | 4.593 | 2.959 | 62.420      | 3.0          | [39],[30]  |
from 0 to $-8.269\ \text{eV}$ are also because of the mixing of atomic orbitals and this results in more covalent bonding between Ti and O in fluorite TiO$_2$. Engaged energy states are from $-20$ to $-16.66\ \text{eV}$, $-8.22$ to $-0.882\ \text{eV}$ and $0.190\ \text{eV}$ to $1.26\ \text{eV}$ in the range of energy from $-20\ \text{eV}$ to $10\ \text{eV}$. In the conduction band, the highest peaks occur due to Ti 3d contributions. Lowest of the valence bands start well before -20eV and it is the result of O 2s state contribution. Highest occupied valence band for fluorite TiO$_2$ is the result of atomic mixing of oxygen 1s and titanium 2p states. 1s of titanium also contribute to the formation of the highest valence band, but its contribution is very less compared to Ti 2p and O 1s states. In the valence band, the highest peaks are the results of the atomic mixing of O p and O s state. Ti 2p, Ti 3d and O 2p contributed a little in the formation of the valence band.

From the band diagram of pyrite TiO$_2$, it can be observed that Fermi energy is more close to the conduction band. Valence band Maxima and conduction band minima lie at different points G and R in the energy band.
implying pyrite TiO$_2$ to be of indirect bandgap having a value of 1.369 eV. Figure 3(c) represents the band structure while figure 3(d) represents TDOS of pyrite TiO$_2$. 17 bands are having a width equal to 6.044 eV below the Fermi level. These bands are as a result of the mixing of atomic orbitals O 2p and Ti 3d. Again 10 bands are having a width of 5.034 eV above the Fermi level. These bands result from the contribution of Titanium 3d shell and Oxygen 2s shell. It is observed from figure 3(d) highest (peak) points occur on the top of valence and bottom of conduction band at $-5.91$ eV, $-3.15$ eV, $-2.3$ eV and $1.10$ eV, $2.03$ eV, $5.08$ eV due to mixing of atomic orbitals Ti 3d and O 2p respectively. Occupied states between O 2p and Ti 3d ranging from 0 to $-7.175$ eV are also because of the mixing of atomic orbitals which indicates a more covalent bonding between Ti and O in pyrite TiO$_2$.

The associated energy states are from $-20.28$ to $-16.66$ eV, $-7.216$ to $-1.251$ eV and $0.118$ eV to $2.48$ eV, $3.05$ to $5.41$ eV in the range of energy from $-20$ eV to $10$ eV. In the conduction band, the highest peaks occur because of Ti-3d contributions and a very less contribution from O 2p. Lowest of valence band starts from $-20$ eV and it is the result of O 2s state contribution. The highest occupied valence band for pyrite is the result of the atomic mixing of oxygen 1s and titanium 2p states. Titanium 1s also contribute to the formation of the highest valence band, but its contribution is very less compared to Ti 2p and O 1s states. In the valence band, major peaks are the results of the atomic mixing of O 2p and O 2s state. A small contribution of Ti 2p, Ti 3d and O 2p are there in the formation of the valence band. From the density of states, it is clear that the width of the conduction band and valence band in pyrite is smaller than fluorite, which supports a larger bandgap value of pyrite as compared to fluorite. This can be verified also from computed results.

From the band diagram of anatase TiO$_2$, it can be observed that Fermi energy is more close to the valence band. Valence band maxima and conduction band minima lie at different points X and G in the energy band implying anatase TiO$_2$ to be of indirect bandgap having a value of 2 eV. Bandgap value obtained using MGGA-TBO9 is 3.3 eV which is 3% higher than experimental value [30]. Figure 3(e) represents the band structure while figure 3(f) represents the TDOS for anatase TiO$_2$. Bands below the Fermi level are having a width equal to 4.13 eV. These bands are as a result of the mixing of atomic orbitals O 2p and Ti 3d. Bands above the Fermi level are having a width of 5.46 eV. These bands result from the contribution of Titanium 3d shell and Oxygen 2s shell. It is observed from figure 3(f) highest (peak) points occur on the top of valence and bottom of conduction band at $-16.22$ eV, $-5.082$ eV and $3.04$ eV, $11.43$ eV due to mixing of atomic orbitals Ti 3d and O 2p respectively. In the valence band, major peaks are the results of the atomic mixing of O 2p and O 2s state. A small contribution of Ti 2p, Ti 3d and O 2p are there in the formation of the valence band.

Figure 3(g) represents the band structure and 3(h) represents the TDOS for rutile TiO$_2$. From the band diagram of rutile TiO$_2$, it can be observed that Fermi energy is more close to the valence band whereas the minima energy point of the conduction band and maxima energy point of valence band lie on the same line G, implying a direct bandgap having a value of 1.81 eV. Bandgap value obtained using MGGA-TBO9 is 2.98 eV which is 0.6% lower than experimental value [30]. Bands below the Fermi level are having a width equal to 5.95 eV. These bands are as a result of the mixing of atomic orbitals O 2p and Ti 3d. Bands above the Fermi level are having a width of 6 eV. These bands result from the contribution of Titanium 3d shell and Oxygen 2s shell. It is observed from figure 3(f) highest (peak) points occur on the top of valence and bottom of conduction band at $-17.45$ eV and $2.435$ eV due to mixing of atomic orbitals Ti 3d and O 2p respectively. In the valence band, major peaks are the results of the atomic mixing of O 2p and O 2s state. A small contribution of Ti 2p, Ti 3d and O 2p are there in the formation of the valence band.

### 3.3. Effective mass of electron and hole ($m^*$)

It is the mass of charge carriers (e$^-$/$h^+$) when they respond to any type of interaction in a crystal lattice. The effective mass highly depends on the crystal structure or electronic band structure in solids [33]. It is usually stated in the unit of the rest mass of an electron, $m_e$ ($9.11 \times 10^{-31}$ kg). Equation (1) represents, the transfer rate of photogenerated electrons and holes which is inversely proportional to effective mass.

$$\nu = \frac{h k}{m^*} \tag{1}$$

Where, $m^*$ represents an effective mass of (e$^-$/h$^+$), k is the wave vector, $h$ is Planck constant, $\nu$ is the transfer rate of photogenerated electrons and holes. Thus, a smaller effective mass is desired to get higher photocatalytic activity. Effective mass is usually calculated using equation (2) and is represented as

$$m^* = h^2 \left(\frac{dE}{dk^2}\right)^{-1} \tag{2}$$

Where, $E$ is the energy of an electron at wavevector $k$ in that band. Table 2 gives a comparison of the calculated effective mass of cubic TiO$_2$ with an effective mass of other phases of TiO$_2$. From table 2, $m^*$ of an electron in pyrite is smaller than fluorite and brookite but it is higher than anatase and rutile. The transfer rate of hole and electrons in pyrite is faster than fluorite. This leads to higher photocatalytic activity in pyrite than fluorite. Also,
pyrite is an indirect bandgap semiconductor, therefore conduction band minima and valence band maxima lies at different \( k \) points. Thus, a lifetime of photogenerated electron and hole increases in pyrite compared to fluorite. This is in agreement with [33], that indirect bandgap semiconductor has better photocatalytic activity than direct bandgap semiconductor.

### 3.4. Optical properties

The optical properties are calculated by considering energy level up to the phonon energy, (40 eV), for cubic phases and (12 eV) for tetragonal phases using GGA-PBESOL. MGGA-TB09 is used to calculate optical properties of normal pressure phases of TiO\(_2\). For calculating the optical properties, equations given in ref [33] are used. As the dielectric function is a complex quantity and so it contains real and imaginary parts. The real part gives an idea about the electronic polarizability of material and the imaginary part gives an idea about the absorption of the material. For evaluating dielectric function Kubo–Greenwood formalism [55, 56] has been implemented. From figures 4(a), (b) and figures 5(a), (b) the value of the \( \varepsilon_1(0) \) for fluorite, pyrite, anatase and rutile TiO\(_2\) are found to be 8.82, 8.17, 6.9 and 8 respectively using GGA-PBES. The value of \( \varepsilon_1(\omega) \) for normal pressure phases are in good agreement with experimental data [57, 58]. Using MGGA-TB09, \( \varepsilon_1(0) \) for anatase and rutile TiO\(_2\) is found to be 5.794 and 5.913 which are very close to experimental value [40, 59]. The highest peak of \( \varepsilon_1(\omega) \) occurs at 3.13 eV for fluorite, 2.27 eV for pyrite, 3.14 eV for anatase and 2.68 eV for rutile. These peaks are the effect of titanium 3d and oxygen 2p states contributions. The refractive index gives an idea about the optical density of the medium. If its value is large then it implies that speed of light is less i.e. density is more. The refractive indices of anatase, rutile, fluorite and pyrite are 2.627, 2.828, 2.98 and 2.85 respectively. Refractive index of anatase and rutile using MGGA-TB09 are 2.407 and 2.469 respectively, which are close to experimental data [41, 42]. From the observed data, we can say that dielectric function is equal to the square of the refractive index. The refractive index is a complex quantity and the extinction coefficient \( k(\omega) \) represents its imaginary part. It gives an idea about light absorption. Figures 4(c), (d) and figures 5(c), (d) shows the plot of \( n(\omega) \) for high pressure and normal pressure phases TiO\(_2\) whereas figure 4(e), (f) and figure 5(e), (f) shows the plot of \( k(\omega) \) for anatase, rutile, fluorite and pyrite TiO\(_2\) respectively. From figures 4(g), (h) and figures 5(g), (h) a sharp decline in reflection spectra can be observed at 9.37 eV for anatase, 7.70 eV for rutile, 14.017 eV for fluorite and 13.096 eV for pyrite. Again, from the figures 4(g), (h) and (g), (h) it is evident that fluorite, pyrite, anatase and rutile reflect around 24.5%, 23.4%, 20.1% and 22.8% of the incident light radiation. Using MGGA-TB09 value of \( R(0) \) is 0.17 and 0.179 respectively. The \( L(\omega) \) is the loss of energy of electrons when they pass through a uniform dielectric material. Here the energy peaks of \( L(\omega) \) occur at 14 eV for fluorite and 13 eV for pyrite. Energy peaks of the loss function and a sharp decline in reflection spectra are matching towards each other for all the structure which is represented by figures 4(m), (n) and figures 5(m), (n) for fluorite, pyrite, anatase and rutile TiO\(_2\) respectively. Figures 4(i) and (j) represent absorption spectra Versus energy for fluorite and pyrite TiO\(_2\) respectively. Figures 5(i) and (j) represent absorption spectra Versus energy for anatase and rutile TiO\(_2\) respectively. Figures 4(k), (l) and figures 5(k), (l) represent absorption spectra Versus wavelength for fluorite, pyrite, anatase, and rutile respectively. It gives an idea about the penetration of the light of a particular \( \lambda \) into the material before it is absorbed. The fluorite is having a more absorptive transition in the visible region than the pyrite. Major peaks of the \( R(\omega) \) occur in the same energy limit as \( \alpha(\omega) \) for all the structures. In the case of fluorite, major peaks occur within the energy range of 0 to 15 eV for both reflection and absorption spectra whereas, it occurs within the energy range of 0 to 14 eV for pyrite TiO\(_2\). As high pressure and normal pressure phases of TiO\(_2\) are behaving as direct and indirect bandgap semiconductor, when the bombardment of a photon with energy greater than bandgap energy takes place, it results in the creation of electron-hole pairs and this phenomenon is known as photoconductivity. This process is important for solar cell application as it involves the conversion of non-electrical energy into electrical energy. Photoconductivity is directly proportional to dielectric function. This relationship is very much apparent from figure 4(a)–(b), figures 5(a)–(b) and figures 4(o)–(p), figures 5(o)–(p). Figures 4(o), (p) and figures 5(o), (p) represent photoconductivity for fluorite, pyrite, anatase and rutile TiO\(_2\) respectively. The absorption of phonon is directly proportional to electrical conductivity. Both fluorite and pyrite have very

| Phase          | The effective mass of the electron (m*) | The effective mass of hole (m*) |
|----------------|----------------------------------------|-------------------------------|
| Fluorite [This work] | 0.514 (average of m* from Γ to R and Γ to M) | 0.1205 (average of m* from Γ to R and Γ to M) |
| Pyrite [This work] | 0.3195 (average of m* from Γ to R and Γ to M) | 0.4225 (average of m* from Γ to R and Γ to M) |
| Anatase [33]    | 0.0948 (average of m* from G to Z and G to M) | 0.1991 (average of m* from B to G and B to M) |
| Rutile [33]     | 0.0948 (average of m* from G to Z and G to M) | 0.5620 (average of m* from G to Z and G to M) |
| Brookite [33]   | 1.4610 (m* from G to Z)                  | 0.4345 (m* from G to Z)        |
good absorption value which ranges from 0 to 15 eV of photon energy for fluorite and 0 to 14 eV for pyrite TiO$_2$. Therefore, cubic TiO$_2$ can provide good electrical conductivity. Table 3 represents the comparison of calculated $\varepsilon_1(0)$, $\eta(0)$ and $R(0)$ with previously reported data. From reflectivity spectra, it is found that TiO$_2$ can provide good electrical conductivity and very much suitable as a coating material.
Figure 5. anatase TiO$_2$: (a) $\varepsilon(\omega)$, (c) $\eta(\omega)$, (e) $k(\omega)$, (g) $\alpha(\omega)$, (i) $\alpha(\omega)$ Vs wavelength, (m) photoconductivity, (o) $L(\omega)$ Rutile TiO$_2$: (b) $\varepsilon(\omega)$, (d) $\eta(\omega)$, (f) $k(\omega)$, (h) $R(\omega)$, (j) $\alpha(\omega)$, (l) $\alpha(\omega)$ Vs wavelength, (n) photoconductivity, (p) $L(\omega)$. 
3.5. Mechanical properties

Mechanical properties give an idea about the nature of forces acting in solids, phonon spectra, and interatomic potential and thereby specifying its hardness, stability, etc. Before doing all the calculations we checked positive definiteness of stiffness matrix \[ \begin{bmatrix} 43, 61 \end{bmatrix} \] using equation (3) for cubic phase,

\[ \begin{vmatrix} c_{11} & c_{12} & c_{13} \\ c_{12} & c_{44} & c_{66} \\ c_{13} & c_{66} & c_{44} \end{vmatrix} = 0, \quad \text{(3)} \]

Tetragonal phase will be mechanically stable, if it satisfies the Born–Huang criteria \[ \text{[62]} \]

\[ \begin{vmatrix} 43, 61 \end{vmatrix} \]

If equation (3) is fulfilled by cubic material then it is considered as mechanically stable and if equation (4) is fulfilled by tetragonal material then it is considered as mechanically stable. Table 4 gives a comparison of calculated elastic properties with previously reported data. Elastic compliance \( s_{ij} \) are calculated using equations given in \[ \text{[63]} \]. Table 5 shows the comparison of Elastic compliance \( s_{ij} \) for fluorite, pyrite, anatase and rutile TiO\(_2\) with available theoretical data. From table 4, it is apparent that cubic and tetragonal phase TiO\(_2\) satisfies respective equations (3) and (4) and hence they are mechanically stable.

Again, Bulk and shear moduli are used to measure the hardness of the material. Two different theories are there to calculate the bulk and shear modulus namely, Reuss theory \[ \text{[67]} \] and Voigt theory \[ \text{[68]} \]. According to Reuss Theory \( B_R \) and \( G_R \) are given by

\[ B_R = (3s_{11} + 6s_{12})^{-1} \quad \text{and} \quad G_R = 5(4s_{11} - 4s_{12} + 3s_{44})^{-1} \]

Where, \( s_{11}, s_{12}, \text{and} \ s_{44} \) are the compliance matrix elements of cubic TiO\(_2\). According to Voigt Theory \( B_V, G_V \) is given by

\begin{table}
\caption{Comparison of calculated \( \varepsilon_1(0), \eta_0(0) \) and \( R(0) \) of fluorite, pyrite, anatase and rutile TiO\(_2\) with previously available data.}
\begin{tabular}{|l|c|c|c|c|c|}
\hline
Phase & Method & \( \varepsilon_1(0) \) & \( \varepsilon_2(0) \) & \( \eta_0(0) \) & \( R(0) \) & References \\
\hline
Fluorite & GGA-PBE-SOL & 8.82 & 2.98 & 0.245 & This work \\
 & GGA-PBE-SOL & 7.64 & 2.76 & -- & \text{[23]} \\
 & GGA-RPBE & 7.72 & 2.78 & -- & \text{[23]} \\
 & GGA-WC & 7.67 & 2.77 & -- & \text{[23]} \\
 & GGA-PW91 & 7.70 & 2.77 & -- & \text{[23]} \\
 & LDA-PZ-OLCAO & 4.7 & 2.2 & -- & \text{[32]} \\
 & LDA & 7.348 & 2.711 & -- & \text{[6]} \\
Pyrite & GGA-PBE-SOL & 8.17 & 2.85 & 0.234 & This work \\
 & GGA-PBE-SOL & 7.46 & 2.73 & -- & \text{[23]} \\
 & GGA-RPBE & 7.42 & 2.72 & -- & \text{[23]} \\
 & GGA-WC & 7.46 & 2.73 & -- & \text{[23]} \\
 & GGA-PW91 & 7.44 & 2.73 & -- & \text{[23]} \\
 & LDA-PZ-OLCAO & 3.75 & 1.90 & -- & \text{[32]} \\
 & LDA & 7.345 & 2.710 & -- & \text{[6]} \\
Anatase & GGA-PBE-SOL & 6.87 & 6.96 & 2.627 & 0.201 & This work \\
 & MGGA-TB09 & 5.828 & 5.727 & 2.407 & 0.179 & This work \\
 & GGA & 6.75 & 6.44 & -- & -- & \text{[26]} \\
 & mBJ & 5.35 & 5.21 & -- & -- & \text{[26]} \\
 & BSE & 5.12 & 4.98 & -- & -- & \text{[37]} \\
 & GGA + \text{U}d + \text{UP} & 6.137 & 5.995 & 2.313 & -- & \text{[38]} \\
 & Exp & -- & -- & 2.3 & -- & \text{[41]} \\
 & Exp & 5.8 & 5.4 & -- & -- & \text{[59]} \\
 & Exp & 6.55 & 6.20 & -- & -- & \text{[57]} \\
Rutile & GGA-PBE-SOL & 7.53 & 8.94 & 2.828 & 0.228 & This work \\
 & MGGA-TB09 & 5.716 & 6.864 & 2.469 & 0.179 & This work \\
 & GGA & 7.34 & 8.68 & 2.79 & -- & \text{[26]} \\
 & mBJ & 5.75 & 6.70 & 2.46 & -- & \text{[26]} \\
 & BSE & 5.71 & 7.33 & -- & -- & \text{[37]} \\
 & GGA + \text{U}d + \text{UP} & 6.298 & 5.485 & 2.605 & -- & \text{[38]} \\
 & Exp & -- & -- & 2.6 & -- & \text{[42]} \\
 & Exp & -- & -- & 2.55 & -- & \text{[60]} \\
 & Exp & 5.7 & 7.0 & -- & -- & \text{[40]} \\
 & Exp & 6.84 & 8.43 & -- & -- & \text{[58]} \\
\hline
\end{tabular}
\end{table}
According to the Hill [69] approximation, the bulk modulus $B_{\text{Hill}}$ and shear modulus $G_{\text{Hill}}$ is given by

$$B_{\text{Hill}} = \frac{(B_{\text{R}} + B_V)}{2}, \quad G_{\text{Hill}} = \frac{(G_{\text{R}} + G_V)}{2}$$

(7)

While Vicker’s hardness [70] is also used to check the hardness of the material and it is given by

$$H_V = 2(k^2G)^{0.585} - 3$$

(8)

Obtained Vicker’s hardness show that rutile is harder than other three polymorphs of TiO$_2$ where, $k = G/B = $ Pugh’s modulus ratio. Young’s modulus is the measure of the stiffness of the material and it is given by

$$E = \frac{9BG}{G + 3B}$$

(9)

Poisons ratio ($v$) is used to classify material and to check the ductile and brittle property of the material. $v = 0.25$ [71, 72] for ionic material $v =$ small approximately equal to 0.1 [69, 73] for covalent materials. For brittle material, $v<0.33$ and for ductile material $v>0.33$. Poisons ratio ($v$) [69, 73] is given by

$$v = \frac{1}{2} \left[ \frac{B - \left(\frac{2}{3}\right)G}{B + \left(\frac{1}{3}\right)G} \right]$$

(10)
Table 6. Mechanical properties of cubic TiO$_2$: B, G, E, \( \lambda \) are in (GPa) and Hv, A, \( \nu \), (B/G) are dimensionless parameters.

| Phase   | Method               | B    | A    | G    | B/G  | E    | \( \nu \) | Hv   | \( \lambda \) |
|---------|----------------------|------|------|------|------|------|---------|------|-------------|
| Fluorite| GGA-PBES [This work] | 269.19 | 0.092 | 81.5 | 3.30 | 222.14 | 0.3626 | 3.48 | 214.84 |
| Pyrite  | GGA-PBES [This work] | 259.08 | 0.735 | 108.57 | 2.38 | 285.8 | 0.316 | 8.22 |          |
|         | GGA-PW91 [31]        | 262.11 | —     | 103.4 | —    | 320   | 0.30   | —   | —           |
|         | OLCAO-PZ [25]        | 244   | —     | 108   | —    | 283   | 0.306  | —   | —           |
|         | GGA [6]              | 296.2  | 0.19  | 68.1  | —    | 431.03 | 0.393  | 1.23 | —           |
|         | GGA [34]             | 249.1  | —     | 84.4  | —    | 227.5 | 0.348  | —   | 192.8       |
|         | Exp [44]             | 202   | —     | —     | —    | —     | —      | —   | —           |
| Anatase | OLCAO-PBES This work | 259.08 | 0.735 | 108.57 | 2.38 | 285.8 | 0.316 | 8.22 |          |
|         | GGA-PBESOL [35]      | 194.19 | —     | 71.03 | 2.73 | 189.93 | —      | 10.47 | —           |
|         | GGA-PW91 [31]        | 192   | —     | 62    | 3.12 | 167   | —      | —   | —           |
|         | GGA [34]             | 182.9  | —     | 58.5  | 3.126 | 158.6 | 0.355  | —   | 143.9       |
|         | GGA-PBESOL [27]      | 191   | —     | 56    | 3.43 | 152   | 0.37   | —   | —           |
|         | OLCAO-PZ [29]        | 198.07 | 0.3   | 45    | 4.3  | 177   | 0.39   | —   | —           |
|         | EXP [2]              | 179   | —     | —     | —    | —     | 0.555  | —   | —           |
| Rutile  | OLCAO-PBES [This work] | 222.04 | 6.22  | 99.75 | 2.225 | 260.29 | 0.304  | 11.383 | 260.29     |
|         | GGA-PBES [35]        | 224.67 | —     | 124.87 | 1.80 | 316.06 | —      | —   | —           |
|         | GGA-PW91 [31]        | 217   | —     | 128   | 1.70 | 320   | —      | —   | —           |
|         | GGA [34]             | 205.2  | —     | 110.5 | 1.857 | 281.1 | 0.272  | —   | 131.5       |
|         | GGA-PBESOL [27]      | 229   | —     | 109   | 2.10 | 281   | 0.29   | —   | —           |
|         | Exp [74, 75]         | 212.235 | —     | —     | —    | —     | —      | —   | —           |

From the calculated \( \nu \), we can say that all the four structures are ductile in nature. If \( A = 1 \), the material is isotropic else the material is anisotropic. Anisotropy \( (A) \) of material is calculated using equation (11) for cubic phase and equation (12) for tetragonal phase

\[
A = \frac{2c_{44}}{(c_{11} - c_{12})} \quad (11)
\]

\[
A = \frac{2c_{66}}{(c_{11} - c_{12})} \quad (12)
\]

From calculated A, it is clear that all the structures are anisotropic in nature. Lame constant \( (\mu, \lambda) \) are calculated using the following equation

\[
\lambda = \frac{\mu E}{[(1 + \nu)(1 - 2\nu)]} \quad (13)
\]

Table 6 gives a comparison of calculated mechanical properties with previously reported data.

4. Conclusion

This paper presents a comparative study on the optical, mechanical, structural and electronic properties of normal and high pressure phases of TiO$_2$ using OLCAO-GGA-PBE-SOL for the first time. MGGA-TBO9 results on electronic and optical properties of normal pressure phases of TiO$_2$ are also analyzed. The computed results are then compared with the previously reported experimental and theoretical data. From the comparison, we can find that lattice constant for anatase and rutile vary only by 0.4% from experimental data [39] whereas it shows 1.3% variation with experimental data for fluorite [11]. However results are much better than the theoretical data [6, 25, 33, 34]. Bandgap values calculated using OLCAO-GGA-PBE-SOL for all the phases of TiO$_2$ are consistent with other theoretical data but underestimated compared to experimental data [30]. Bandgap values obtained using MGGA-TBO9 is the approximation of experimental data [30]. Effective mass analysis of cubic TiO$_2$ shows that transfer rate is faster in pyrite and hence exhibits higher photocatalytic activity than fluorite. Dielectric constant value calculated using OLCAO-GGA-PBE-SOL for all the structure are higher than other theoretical data [6, 23, 26, 32, 38]. Dielectric constant value for anatase and rutile using GGA-PBES are close to the experimental value [57, 38]. Dielectric constant and refractive index calculated using
MGGA-TB09 for anatase and rutile are very much close to experimental data [40, 41, 59, 60] and better than [26, 37, 38]. Elastic constant of rutile TiO2 are in excellent agreement with experimental data [65]. Obtained bulk modulus value for anatase, rutile and fluorite vary by 2%, 4.7% and 33% from experimental data [2, 44, 74] and better than [27, 29, 31, 35]. As experimental data of pyrite TiO2 is not available, obtained properties are compared with other theoretical data and results are found to be consistent with previously reported data.

OLCAO-GGA-PBE-SOL provides better results for structural and mechanical properties of normal pressure phases compared to high pressure phases. MGGA-TB09 results on optical and electronic properties are the approximation of experimental data. This comparative analysis of TiO2 using OLCAO-GGA-PBE-SOL and MGGA-TB09 will be helpful for future theoretical as well as experimental investigations. This analysis can be also helpful to study various properties of other material using the two methods described earlier.

5. Future scope

Among many candidates for photo-catalysts, TiO2 is the only material suitable for industrial use because of its efficient photoactivity, the highest stability and lowest cost. Also it is suitable for solar cell applications. Both these applications required small bandgap material. But TiO2 exhibits large bandgap value. So, to make it suitable for above application one need to narrow the the bandgap using suitable metal and non-metal doping. So, one can verify the properties of doped and undoped TiO2 using two methods mentioned in this paper. This will help to find its future applications.

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