Science World Journal Vol. 14(No 3) 2019
www.scienceworldjournal.org
ISSN 1597-6343
Published by Faculty of Science, Kaduna State University

ELECTRONIC BAND STRUCTURE AND OPTICAL PROPERTIES OF TITANIUM DIOXIDE

H. Nura[1], S.G. Abdu[2], A. Shauibu[3] and M.S. Abubakar[4]

[1,2,3,4] Department of Physics, Kaduna State University, Kaduna. PMB 2339, Kaduna, Nigeria

Authors Email Addresses: [1]halima.nura@kasu.edu.ng, [2]sgabdul@kasu.edu.ng, [3]alhazikara@gmail.com, [4]msbakarhtc@gmail.com

ABSTRACT

In this work the Fritz-Haber Institute *ab initio* Molecular Simulation (FHI-aims) code was used to investigate and obtain the band energies and linear dielectric functions of the three naturally occurring phases of TiO_2 (Rutile, Anatase and Brookite). The exchange-correlation interactions are treated by the PBE. The results of the band gap were obtained to be 1.76 eV for Rutile, 2.07 eV for Anatase and 2.33 eV for Brookite with Rutile having a direct band gap and indirect band gaps for both Anatase and Brookite. The obtained band gaps are in agreement with other theoretical work, especially on the rutile phase. The linear dielectric function was calculated using Random Phase Approximation (RPA) where the average static dielectric function at ω= 0 was obtained as 5.61 for Rutile TiO_2, 4.29 for Anatase TiO_2 and 2.23 for Brookite TiO_2.

Keywords: Rutile, Anatase, Brookite, Density Functional Theory, FHI-aims, Band gap energies, Dielectric Constant

INTRODUCTION

Recently there has been many breakthroughs in Nanotechnology. Research in Nano particle offers wide scope in the development of new and improved solutions in different fields such as medicine, cosmetics, food, optics and electronics. Nanotechnology is present in our everyday activities; in our homes, in paints, cosmetics, food dyes, UV protection, computers, medicine and renewable energy (solar cells). This is true for Titanium dioxide (TiO_2) as it is used in paints, deodorants and others.

TiO_2 is known to be a semi-conductor with a large optical reflectivity at visible light, it is a strong absorber of UV rays and highly photoactive, and it reacts well with other chemical agents (Auvinen, 2013). Owing to these properties TiO_2 is mostly used as food colouring, white pigment in paints and pharmaceutical product, sunscreens to block UV rays, cosmetics, plastics and ceramics. It shows encouraging applications in batteries, solar cell technology, UV protectors, nano sensors as well as biomedical applications like photodynamic therapy for cancer, genetic engineering, etc. All these properties make it a very interesting compound. Better understanding of its properties is necessary for these modern applications of TiO_2. It forms three distinct crystal structures; Rutile, Anatase and Brookite. Anatase and Rutile structures are tetragonal, which is as a result of a slight difference in the angles and bond lengths between the atoms. Each of them has a different space group and lattice constant. Brookite however, has a complicated orthorhombic structure.

TiO_2 has been studied since its discovery in 1791, it occurs naturally as an oxide of titanium. It is known to be a semiconductor with an experimental bandgap of 3.0 eV for Rutile and 3.2 eV for Anatase (Auvinen, 2013). It is a widely investigated oxide due to its numerous applications from photocatalysis (Fujishima, 1967), photovoltaic (Gratzel, 2005), optical coating (Sankapal *et al*., 2005) etc. All these new and improved applications of TiO_2 call for better understanding of its properties, especially optical and electronic. Many of its properties have been investigated both theoretically and experimentally especially on the Rutile phase which is the most stable form of the polymorphs (Faruque *et al.,* 2010; Shehap & Dana, 2015). There are some ongoing investigations on the Anatase phase while Brookite is still under research even experimentally. The Rutile and Anatase phase have been extensively studied compared to the Brookite form (Dutta *et al.,* 2000). This may be because it is computationally expensive due to the number of atoms in its unit cell and its difficulty in preparation (Dambournet *et al.,* 2010). Some of its important properties, for instance the optical property, electronic bandgap are still under deliberation. Thus, there is need for more research into their properties most especially on the Brookite phase for better understanding on this phase and its potential application. Therefore, this work will /calculate and present computational details and results of the electronic band structure and optical dielectric tensor of the 3 naturally occurring forms of TiO_2.

MATERIALS AND METHOD

Density Functional Theory (DFT)

DFT is a common technique used to study important properties of materials using computational method. It is a successful approach to finding solutions to the fundamental equation that describes the quantum behaviour of atoms and molecules. It is based on the idea that all the ground state properties of the system of interacting particles can be derived from the ground state electron density *n*(**r**) of the system. In 1964, Hohenberg and Kohn formulated DFT as an exact theory of many-body systems:

"*For a system of interacting particles in an external potential, the external potential* $V_{ext}(r)$*is uniquely determined by the ground state density*$n(r)$. And *For any external potential* $V_{ext}(r)$, *we can define a universal functional or energy E[n] in the terms of density n(**r**), and the minimum for E[n] as a function of n(**r**) represents the exact ground state and the ground state density of the system*" (Martin 2014).

$$n(r) = N\int |\Psi(r, r_2, r_3 \dots . r_N)|^2 dr, dr_2 \dots . dr_N \qquad (1)$$

The energy functional can now be formulated as

$$E_{HK} = T[n] + \int V_{ext}(r)\, n(r)\, d^3r + E_{11} \qquad (2)$$

where T[*n*] is the internal kinetic energy of the system, $V_{ext}(r)$

the external potential energy, and E_{11} represents the interaction energy of the nuclei.

In 1965, Kohn and Sham proposed an alternative approach and suggested that the complicated many-body problem can be replaced with an auxiliary independent-particle problem, which can be solved far more easily. This is based on the assumption that:

"*The exact ground state of the system can be represented by the ground state of the auxiliary system of non-interacting particles and The auxiliary Hamiltonian can be selected so that it has a usual kinetic energy operator and an effective local potential V eff (**r**), which acts on the electron in the point **r**, having a spin of*" σ (Martin 2014).

Using the Kohn-Sham approach, the Hohenberg-Kohn expression can be written as

$$E_{KS} = T_s[n] + \int V_{ext}(r)n(r)dr + E_{Hartree}[n] + E_{11} + E_{xc}[n] \qquad (3)$$

$T_s[n]$ is the kinetic energy functional, $E_{Hartree}[n]$ is the classical Coulomb interaction energy of the electron density interacting with itself, E_{11} is the interaction between the nuclei, $V_{ext}(r)$is the external potential due to the nuclei and any other external fields, and $E_{xc}[n]$represents the exchange-correlation energy including all many-body effects.

The accuracy issues of DFT are strongly depended on the quality of the exchange correlation functional, because the exact exchange-correlation energy is not known generally, various approximations have been developed for the exchange correlation functional. These approximations include (i) Local Density Approximation (LDA), (ii) Generalized Gradient Approximation (GGA) and (iii) Hybrid Approximation. The most common one used is the LDA (Kratzer *et al.,* 1999*;* Qing-Miao *et al.,* 2007; Juarez *et al.,* 2008). In LDA, the exchange correlation energy at each point in the system is the same as that of a uniform electron gas of the same density. Using this approximation, the exchange-correlation energy for a density $n(r)$ is given by

$$E_{xc}^{LDA} = \int n(r)E_{xc}(n)dr \qquad (4)$$

Band Structure

The nature of electrons in solids is described by the band structure. The arrangement of electronic state within bands is one of the closest consequence of periodic structure of crystalline solids. It gives the electronic levels in crystal structures. This band has a particular importance for semiconductors as many properties of semiconductors are determined by only a small number of these bands (Owolabi *et al*., 2016). The band structure is characterized by two quantum numbers, the Bloch vector k, an element in k-space (reciprocal space) and the band index n. the electron energy $E_n(k)$ remains a continuous function of k, so that an endless range of energies is obtained known as the energy bands.

Many electrical, optical and even some magnetic properties of crystals can be explained in terms of the band structure. Band structure theory has been very successful for predicting ground-state properties such as cohesive energies, crystallographic structure, chemical bond lengths and lattice parameters, etc. (Hohenberg & Kohn, 1964; Kohn & Sham, 1965).

Dielectric Function

In bulk solids the complex frequency dependent dielectric function is related to the band structure. From it, all other optical constants like optical conductivity, loss function and reflectivity can be determined. It estimates the ability of a material to interact with electric field and gets polarized by the field.

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 \qquad (5)$$

ε_1 represents the real quantity of the dielectric function and establishes how the photon speed slows down in a material. It is also associated to the stored energy contained in the medium. The imaginary component, $i\varepsilon_2$, reveals how a dielectric material absorbs energy from an electric field owing to motion of dipole (Shehap & Dana, 2015). The dielectric constant, also called relative permittivity, is the value of the real part of the dielectric function at zero frequency i.e. [ϵr (ω = 0)] (Abdulsalam & Babaji., 2018).

FHI-aims

FHI-aims (Fritz Haber Institute *ab initio* molecular simulations) is a computer software package designed for computational materials learning established only on quantum-mechanical first principles (Blum *et al*., 2009). It applies DFT to determine the total energy for the ground state properties and derived quantities of molecules and solids. Additionally, FHI-aims uses different self-energy formalisms like second-order Møller-Plessett (MP2) and (GW) to calculate electron single quasi particle excitation in molecules and total energy calculation based on Hartree-Fock (HF) to calculate the wave function. FHI-aims supports many body perturbation principles like the Random Phase Approximation (RPA), MP2, Density Functional Perturbation Theory (DFPT),Second-Order Screened Exchange (SOSEX), etc. (Blum *et al*., 2009).

FH-aims software works on any Linux operating system. Ubuntu 16.04 LTS was used for this work with a running FORTRAN compiler; Intel's ifort compiler from Intel parallel studio XE was installed and used for the calculations in this work.

The input files needed for FHI-aims to run any calculations are *control.in* and *geometry.in*. These files must be situated in the same directory from which it will be invoked at the terminal. The *control.in* file contains all runtime data; all convergence criteria are set here. The *geometry.in* consist of all data associated to the atomic structure used for a prearranged calculation. For more accuracy, FHI-aims provides pre-constructed default definitions for sub keywords associated with different species (chemical elements) which are useful in regulating all integration grids, the basis set and the accuracy of the Hartree potential. This can be retrieved in the *species_defaults* sub directory of the package and can be added to control.in.

For periodic calculations with FHI-aims, the first thing to do is to create the geometries at the geometry input format (*geometry.in*). Then the basic parameters and convergence criteria are set up in *control.in*.

The geometry optimizations of the bulk Rutile, Anatase and Brookite TiO_2 were carried out to find the most stable structural parameters. The final results of the optimization were used to create a new optimized *geometry.in* file and the electronic band structure and dielectric tensor of the three naturally occurring phases of TiO_2 were calculated along the high symmetry lines of the Brillouin zone by specifying the codes in the *control.in.*

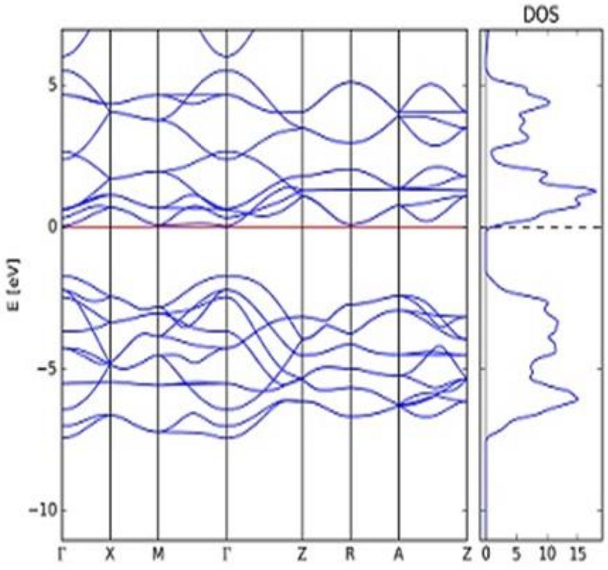
RESULTS AND DISCUSSION

The band structures of bulk Rutile, Anatase and Brookite Titanium dioxide were calculated and plotted using aimsplot.py. The symmetry points are shown by the vertical lines while the position of the Fermi level of these crystals is shown by the zero on the energy scale on the band structure graph. In all three cases, a wide Band gap is noticed, that is the range of energies where there are no electronic states across the entire Brillouin zone. It is noticed that the Fermi level lies within the band gap and the band below the level are fully occupied. This shows a characteristics of a wide band gap semi-conductor.

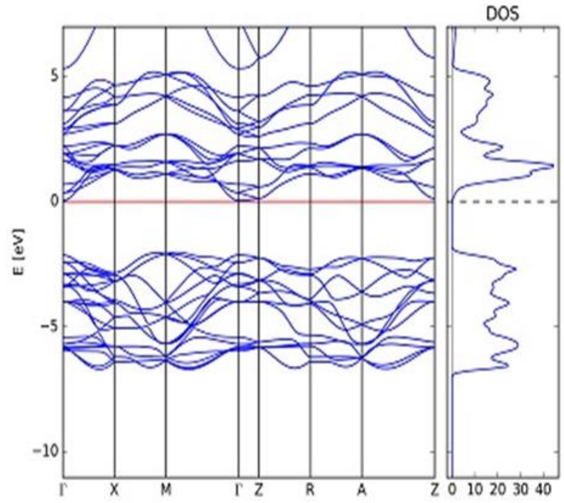
Fig. 1(a) shows the Energy band structure along high symmetry directions in the Brillouin Zone and the corresponding Density of States (DOS) for Rutile TiO_2. The highest occupied molecular orbital (HOMO) at the top of the valence band and the lowest unoccupied molecular orbital (LUMO) at the bottom of the conduction band show a direct electronic band gap of 1.76 eV at Γ point.

From fig. 1(b) above we notice that Anatase TiO_2 has a valence band maximum (VBM) along M point and conduction band minimum (CBM) at Γ point. Since the valence band maximum and the conduction band are on different symmetry points it shows that Anatase TiO_2 is an indirect band gap semiconductor with an energy gap value of 2.07 eV. The calculated energy gaps for Rutile and Anatase TiO_2 are close to the reported band gaps of 1.88 eV and 1.94 eV, respectively (Landman *et al*., 2012).

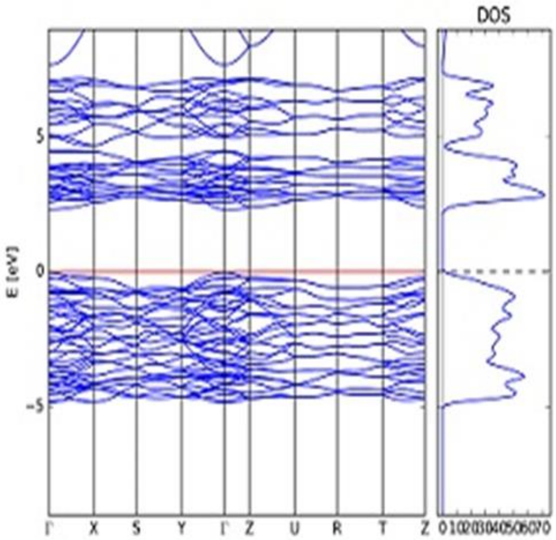
Our calculation shows that Brookite also has an indirect band gap of 2.33 eV along Γ-Z with its VBM on the Γ point and CBM at the Z point.



(a)



(b)



(c)

Figure 1: Band Structure and Density of States (DOS) of (a) Rutile TiO_2 (b) Anatase TiO_2 and (c) Brookite TiO_2

Table 1: Calculated Bandgap Energies for Rutile, Anatase and Brookite TiO_2

Method	Calculated Bandgap (eV)			Theory 1 (Landman *et al*., 2012)			Theory 2 (Labat *et al*., 2007)		
	Rutile	*Anatase*	*Brookite*	Rutile	Anatase	Brookite	Rutile	Anatase	Brookite
PBE	1.76	2.07	2.33	1.88	1.94	1.86	1.88	2.36	-

Table 1 provides the summary comparison of calculated band gaps with other theoretical work. The values show clearly a close relation between the calculated and other theoretical values where available for all the 3 phases of titanium dioxide. The results of the band gap show an underestimation as compared to the experimental band gap of 3.0 eV for Rutile (Tang *et al*., 1995), 3.18 eV for Anatase (Tang *et al*., 1993) with a percentage underestimation of 70% and 53%. This is a known limitation of DFT-GGA approximations in band gap calculations. However, the underestimation of the band gap from the experimental values is mainly due to the fact that the exact functional in the Hohenberg-Kohn theorem is not known. Therefore the comparison of FHI-aims approximations for the exchange correlation predicts closely the band gap when compared to other theoretical values.

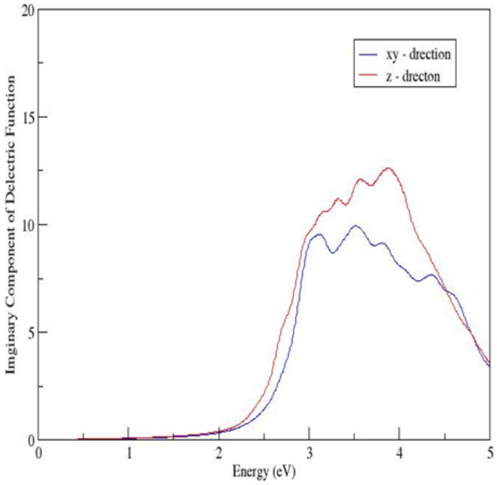
Optical properties

The values for the real components of linear dielectric tensor against frequency for the directions [100], [010] and [001] are shown in table 2. The real component of the dielectric function at zero frequency (ω = 0) gives the dielectric constant (relative permittivity). For both Rutile and Anatase, the dielectric constant (relative permittivity) at the [100] and [010] directions have the same value, while the ones obtained at [001] directions are higher than the ones at [100] and [010] directions.

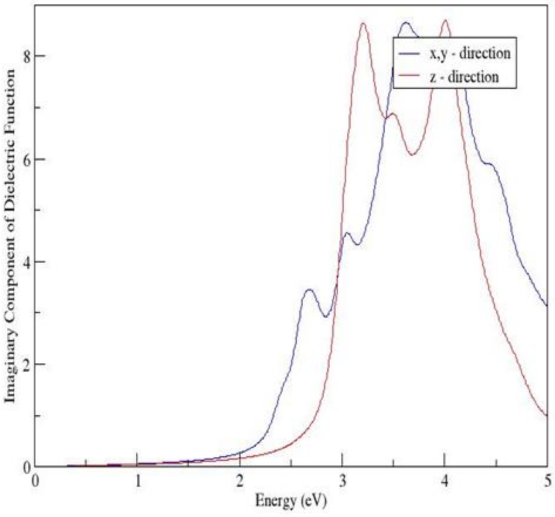
Table 2: Calculated Dielectric Constant for Rutile, Anatase and Brookite TiO_2

Crystal Phase	Re [$\varepsilon_r\ (\omega = 0)$]		
	[100]	[010]	[001]
Rutile	5.27	5.27	6.29
Anatase	4.34	4.34	4.20
Brookite	2.20	1.92	2.58

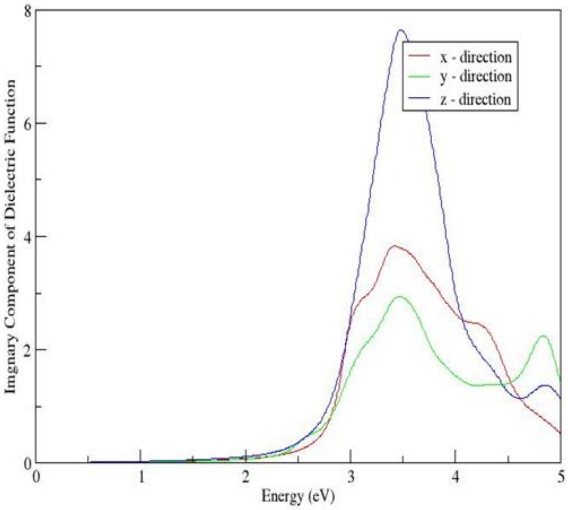
The graph of imaginary components of linear dielectric tensor against frequency for the directions [100], [010], and [001] are shown in Fig. 2. The imaginary quantity shows the absorption spectrum with peaks at different values of the energy. Fig. 2(a) shows the imaginary part of the dielectric function for Rutile. It can be seen that there is an increase in the absorption which occur at 1.5 eV with major peaks of 10.5 at 3.13 eV, 12.1 at 3.59 eV and 12.6 at 3.90 eV. The minimum energies obtained for both Anatase and Brookite as seen in fig. 2(b) and 2(c) are 1.0 eV and 1.6 eV respectively with 2 major peaks of 8.64 at 3.21 eV and 8.68 at 4.01 eV for Anatase in the z [001] direction and a major peak of 7.63 at 3.52 eV for Brookite also in the z [001] direction.



(a)



(b)



(c)

Figure 2: Imaginary component of dielectric function for (a) Rutile TiO_2, (b) Anatase TiO_2 and (c) Brookite TiO_2

Conclusion

The results of electronic band structure and optical dielectric function of 3 phases of Titanium Dioxide were presented using Density Functional Theory as implemented in FHI-aims. The energy band structures were determined with Rutile having a direct band gap of 1.76 eV and an indirect band gap of 2.07 eV and 2.33 eV for Anatase and Brookite TiO_2, respectively. This shows significant improvement compared to other theoretical calculations obtained from the work of Landman *et al*. (2012). The optical properties calculation was carried out using Random Phase Approximation (RPA).The dielectric functions for all the three phases were calculated using 12 x 12 x 12 k-points.

REFERENCES

Abdulsalam H. and Babaji G. (2018). First Principle Study on Lead-Free CH3NH3GeI3 and CH3NH3GeBr3 Perovskite Using FHI-aims Code. https://arxiv.org/ftp/arxiv/papers/1806/1806.10945.pdf Accessed 01/07/2018.

Auvinen S. (2013). Computational modeling of the Properties of TiO_2 nanoparticles. .ISSN-L 1456-4491 Cambridge University Press, 1 Ed.

Blum V., Gehrke R., Hanke F., Havu P., Havu V., Ren X., Reuter K. and Scheffler M. (2009). *Ab initio* molecular simulations with numeric atom-centered orbitals. *Computer Physics Communications,* 180: 2175-2196.

Dambournet, D. Belharouak, I. and Amine, K. (2010). Tailored preparation methods of TiO_2 Anatase, Rutile, Brookite: Mechanism of formation and electrochemical properties. *Chem. Materials*. 22(3): 1173-1179.

Dutta P.K., Ginwalla A., Hogg B., Patton B.R., Chwieroth B., Liang Z., Gouma P., Mills M. and Akbar S. (2000). Interaction of CO with Anatase Surfaces at High Temperatures: Optimization of a CO Sensor. *J Phys Chem*. 103:4412-22.

Faruque M.H, Alexander V., Irina V., Janusz N. and Graeme E. (2010). Electronic and optical properties of anatase TiO2 nanotubes. *Computational Materials Science* 48: 854–858.

Fujishima A. and Honda K. (1972). Electrochemical Photolysis of water at a semiconductor electrode. *Nature*, 238, 37—38.

Gratzel, M. (2005). Dye-Sensitized Solid-State Hetero-junction Solar Cells, *Journal of Organic–Based Photovoltaics*, Vol 30, pp. 23-27.

Hohenberg P. and Kohn W. (1964). Inhomogeneous Electron Gas, *Physical Review*, 136. B864.

Juarez L.F., Da Silva I. and Catherine S. (2008). Trends in adsorption of noble gases He, Ne, Ar, Kr, and Xe on Pd (111): All-electron density-functional calculations, *physical review B* 77, 045401.

Kohn W. and Sham L.J. (1965). Self-consistent equations including exchange and correlation effects, *Physical review,* 140(4A), A1133.

Kratzer P., Morgan C.G., Penev E., Rosa A.L., Schindlmayr A., Wang L.G. and Zywietz T. (1999). FHI98MD Computer Code for Density Functional Theory Calculations for Poly-atomic Systems: User's Manual, Program Version 1:03.

Labat F., Domain C. and Baranek P. (2007). Density functional theory analysis of the structural and electronic properties of TiO_2 rutile and anatase polytypes: performance of different exchange correlation. *Journal of chemical physics* 126:154703.

Landmann M.E., Rauls W. and Schmidt G. (2012). The electronic structure and optical response of rutile, anatase and brookite TiO_2. *Journal of physics: condensed Matter: 195503* (6pp).

Martin R.M. (2004). Electronic Structure: Basic Theory and Practical Methods. *Cambridge: Cambridge University Press*, 1 ed.

Owolabi J., M. Y. Onimisi, S.G. Abdu and G.O. Olowomofe (2016). Determination of Band Structure of Gallium-Arsenide and Aluminium- Arsenide Using Density Functional Theory. Computational Chemistry, **4**(03), pp. 73-82.

Qing-Miao, H. Karsten, R. and Scheffler, M. (2007). Towards an Exact Treatment of Exchange and Correlation in Materials: "Application to the CO Adsorption Puzzle" and Other Systems.*Phys. Rev. Lett*. 98, 176103.

Sankapal B.R., Lux-Steiner, M.C. and Ennaoui A. (2005). Synthesis and characterization of anatase-TiO_2 thin films. *Journal of applied surface science*, 239 (2), 165-170.

Shehap A.M. and Dana S.A. (2015). Structural and optical properties of TiO_2 nanoparticles / PVA for different composites thin film,. *Int. J. Nano electronics and Materials* 9, 17-36.

Tang H., Levy F., Berger H. and Schmid P.E. (1995). Urbach tail of Anatase TiO_2. *Phys rev B*, *Condensed Matter*. 52(11), 7771-7744.

Tang H., Berger H., Schmid P.E., Levy F. and Burri G. (1993). Photoluminescence in TiO_2 Anatase single crystal. *Solid state communication*, 87 (9), pp. 847- 850.