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A density functional study of structural, electronic and optical properties of titanium dioxide: Characterization of rutile, anatase and brookite polymorphs

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ABSTRACT

Study of fundamental physical properties of titanium dioxide (TiO_2) is crucial to determine its potential for different applications, such as study of electronic band gap energy is essential to exploit it for optoelectronics and solar cell technology. We present here investigations pertaining to structural, electronic and optical properties of rutile, anatase and brookite polymorphs of TiO_2 by employing state of the art full potential (FP) linearized (L) augmented plane wave plus local orbitals (APW+lo) approach realized in WIEN2k package and framed within density functional theory (DFT). To incorporate exchange correlation(XC) energy functional/potential part into total energy, these calculations were carried out at the level of PW–LDA, PBE–GGA, WC–GGA, EV–GGA, and mBJ–GGA which are exploited as the manipulated variables in this work. From our computations, the obtained structural parameters results were found to be consistent with the available experimental results. The analysis of electronic band gap structure calculations point to TiO_2 as a semiconducting material in all three phases, whereas band gap character around Fermi level was found to be indirect for anatase, and direct for rutile and brookite phases. Density of state (DOS) profiles showed a substantial degree of hybridation between O 2p and Ti 3d in conduction and valence band regions, illustrating a strong interaction between Ti and O atoms in TiO_2 compund. In addition, our investigations of the optical properties also endorse the interband transitions from O 2p in valence band to Ti 3d in conduction band.

1. Introduction

Strong bonding in transition metal oxide compounds, that leads to higher value of heat of formation, wide electronic bandgap along with many other diverse and fascinating properties, has attracted a great deal of attention of material scientists as well as engineers to exploit their potential in advanced applications [1]. Though several oxide materials are used extensively in different state of the art technologies, being functional materials, many investigations these days on oxide materials are particularly carried out to satisfy the requirements of industry and community. Some of the main demands of the industry in finding economical alternative materials are that they should be non-toxic, environmentally friendly, abundantly available and show excellent electronic conductivity/performance as base materials in electronics and

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optoelectronics to fulfill the energy demand of the future [2]. To achieve this goal numerous studies at both experimental and theoretical level have been carried out on the different phases of TiO_2 to comprehend its optoelectronic response.

TiO_2 exists in several polymorphs i.e. rutile, anatase, brookite, columbite, baddeleyite, cotunnite, pyrite and fluorite. Three of these polymorphs exist naturally, while others have to be engineered. Due to their remarkable promising properties and various applications including solar cell technology, flat panel displays, sensors, pigment, catalyst and transparent optoelectronic devices, naturally occurring polymorphs (rutile, anatase and brookite) have been widely synthesized [2–6]. Rutile structure posses the highest stability [7] compared to the others, anatase structure is thermodynamically stable up to 800 °C [8] and brookite structure resembles the properties of the rutile structure [9]. Moreover, TiO_2 is classified among the noteworthy ceramics materials because of its high chemical stability, low cost and non-toxicity [10]. It has been placed among several important materials that add the hydrophobic, hydrophilic, photocatalytic and antibacterial features into traditional ceramic tiles [10–13]. Among the three polymorphs of TiO_2, the anatase structure is the most favorable for photocatalytic applications, and has generated considerable motivation for extensive research on TiO_2. Moreover, extensive applications of TiO_2 have also been extended to air and water purifications [14,15], PVC fabrics, anti-bacterial and self cleaning effects, glass and cultural heritage protection [16–18]. TiO_2 is particularly used for development of functional ceramic tiles [19].

Besides this, TiO_2 has attracted the particular attention of scientists in 1971, when Fushijima and Honda revealed the effect of photo electrochemistry of TiO_2 while using it as an anode. Moreover, it is widely used in diverse applications from pigmentation to solar cells [20–22]. It is also employed in dye-sensitized solar cells as a common photocathode [23]. Wang et al. used TiO_2 to fabricate ultraviolet (UV) photo-detector and reported it to be more efficient than silicon (Si), gallium nitride (GaN) as well as zinc oxide (ZnO) UV photo-detectors [24]. However, in solar cell technology TiO_2 has limited applications due to its wide bandgap semiconductor nature. It is mainly used as a solar window/substrate for the thin film solar cell technology. To unveil its factual potential for further and direct solar cell applications, as well as for optoelectronic devices, capturing of light over entire visible spectrum is crucial and consequently tuning of the fundamental optical bandgap of naturally occurring/synthetic phases is essential. Prior to do so a comprehensive knowledge regarding electronic and optical properties for its naturally occurring phases is crucial from experimental to theoretical level. Experimental work involving TiO_2 has progressed tremendously over the years; however reporting of theoretical work related to the compilation of TiO_2 polymorphs is scarce.

Presently at theoretical level most of the investigations are performed via DFT approaches because DFT provides a simple framework to quantum many body problem and is contributing significantly in designing new materials as well as tuning and investigating different properties of the materials. However, the quality of the DFT calculations depends upon the proper choice of XC energy functional/potential. Although TiO_2 is considered a promising material for high-tech technologies and solar cell applications, in addition to experimental studies, some important first principles DFT studies about it have been reported previously in the literature; Khan et al. reported a DFT study of anatase phase of TiO_2 using a pseudo-potential approach as embodied in CASTEP computational package at the level of PBE–GGA and GGA+U [25]. Similarly, Mo and Ching reported a study of rutile, anatase and brookite phases with first principles OLCAO scheme at the level of local density approximation (LDA) [26]. Landmann et al. investigated electronic and optical properties of rutile, anatase and brookite phases using projector augmented wave (PAW) approach framed within DFT approach implemented in VASP code at the level of hybrid functional (HSE06 and G_0W_0) [27]. Thilagam et al. performed time dependant DFT study of dielectric properties for all three (rutile, anatase, and brookite) naturally occurring polymorphs using BAND package at the level of ALDA [28]. Patrick et al. performed a first principles pseudo-potential DFT study for rutile and anatase phases of TiO_2 at the level of GGA+U by employing Quantum Espresso software [29]. Sai and Bang-Gui presented a study on rutile and anatase phases using DFT–FPLAPW approach at the level Trans-Blaha approach of modified potential (TB–mBJ) [30]. Mahmood et al. studied electronic and optical properties of the rutile and anatase pahses at the level GGA+U by employing pseudo-potential DFT approach as embodied in CASTEP software package [31], most of the previous studies present underestimated/overestimated bandgap values besides giving contradictory nature of bandgap nature as well. Also a comprehensive first principles DFT–FLAPW study for naturally occurring phases (rutile, anatase and brookite) is rarely found in the literature. Moreover, mostly work is at the level of standard LDA/GGA, which is known for their underestimation of bandgap results. Therefore, it is very important to perform study to insight view regarding optoelectronic properties particularly electronic properties with reliable XC approximations.

In this work, we perform a detailed study of the electronic and optical properties of TiO_2 in its three naturally occurring structures of TiO_2 and complete our initial and partly presented results in 27th RCSSST 2013 conference proceedings concerning rutile structure. This study is accomplished by adopting first-principle approach based on DFT implemented within WIEN2k package. Different XC functional of GGAs and PW–LDA are employed as the manipulated variables in this study. We report their optical properties using PBE–GGA and mBJ–GGA functional with parameters of complex dielectric and conductivity function, refractive index and extinction coefficient, reflectivity, absorption coefficient and energy loss spectrum.

2. Methodology

Computational methods presented in this study are based on DFT first-principle approach implemented within the WIEN2k software package [32] at different levels of XC functional. The calculations of structural properties were carried out using LDA (Local Density Approximations) with PW (Perdew and Wang) [33] parameterization, and GGA (Generalized Gradient Approximations) with two different