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Physics

THE ELECTRONIC STRUCTURE AND PHONON PROPERTIES OF RUTILE (TiO_2) CRYSTAL

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Abstract

Titanium dioxide (TiO_2) is a white solid inorganic thermally stable. It is also non-flammable and widely used in the manufacture of many products such as pigments in foodstuffs, paints and cosmetics due to its photo-catalytic applications. It is of low cost but is has high activity. It has been used broad functionality, long term stability and no toxicity. We have performed density functional theory based first principles calculations to study the stability, geometrical structures, electronic and phonon properties of the rutile crystal of TiO_2 within DFT level of approximations. The most stable geometry is considered to study the electronic band structure, density of states, phonon spectrum and phonon DOS. The band gap of our present work is slightly different from the experimental value indicating TiO_2 is a direct band gap insulator.

Keywords: *Electronic and phonon properties, band structure and density of states*

Introduction

Titanium dioxide (TiO_2) is a white solid inorganic substance which is thermally stable, non-flammable and has less solubility (Mishra, 2014). It is the most widely used oxide for photo-catalytic applications due to its low cost and high activity. Titanium dioxide has different nomenclatures like titanium (IV) oxide or titania. TiO_2 can be used as a pigment, which is well renowned as titanium white, Pigment White 6 (PW6) or CI 77891(Tong *et al*. 2013). The transparency and UV absorbance of it allows its effective use as a protective ingredient for sunscreens.

TiO_2 has a broad functionality, long term stability and no toxicity. It is used in the manufacture of many products such as pigments in foodstuffs, paints and cosmetics (Umebayashi *et al*. 2002). Titanium dioxide (TiO_2) nano-materials has numerous and diverse applications. It encompasses the environmental and biomedical applications such as photo-catalytic degradation of pollutants, water purification, bio-sensing and drug delivery (Fujishim *et al*. 1972; Chen and Mao 2007). The study of TiO_2 draws an attention of many scientists and researchers in the last few decades. So, the study of TiO_2 has become a hot cake for the researchers. It possesses the enigmatic physical and chemical properties (Mo and Ching 1995). The interest in photo-catalysis has focused on the use of semiconductor materials as photo-catalysts because of the ability of TiO_2 to oxidize both organic and inorganic substrates in air and water through oxidation and reduction processes (Lbhadon *et al*. 2013). So, TiO_2 emerges out as a better photo-catalyst in heterogeneous photo-catalytic applications.

It has been used in UV induced electron photo-excitation (Islam *et al*. 2007), as pigment in paint and in hydrogen production. It has been used persistently in transparent conducting oxides (Furubayashi *et al.* 2005), photo-catalysts for solar energy utilization and environmental clean- up (Zhang 2002). It is excessively used in the fabrication of anti-reflection coatings, interference filters, optical waveguides (Siefering *et al.* 1990) and gas sensors (Matsui and Akaogi 1991).

Mainly, there are three types of crystal structures of TiO_2 (Matsui and Akaogi 1991; Landmann *et al.*

2012); Rutile crystal: tetragonal (4/mmm), space group : $P4_2$ /mnm-$D^{14}_{4h;}$ Anatase crystal : tetragonal (4/mmm), $I4_1$ /amd -$D^{19}_{4h;}$ Brookite crystal : 4h orthorhombic (mmm), Pbca-$D^{15}_{2h;}$ Only the first two play a significant role in industrial applications. The last type brookite is limited due to its rareness and difficulties in preparation. Among three polymorphs of TiO_2, the rutile TiO_2 surface is relatively easy to prepare and is thermodynamically very stable. Rutile TiO_2 has attracted a lot of interest in the study of transition metal oxides and their properties as well.

Rutile (figure 1) is the most common naturally occurring titanium dioxide polymorph. It is abundantly found in igneous rocks, mantle xenoliths, lunar rocks and meteorites (Meinhold 2010). It is one of the most stable heavy minerals found in the both ancient and modern sediments. Rutile has a wide range of applications in earth sciences.

Although many theoretical calculations of the electronic properties of rutile TiO_2 have been reported earlier, it seems quite interesting that the experimental and calculated values of band gaps in rutile TiO_2 differ in different papers. The experimental value of direct band gap differs mainly due to the use of different approximations in the electronic properties calculations. This discrepancy in the band gap calculation makes rutile TiO_2 a hot topic for discussion. In this work, we consider the rutile TiO_2 to study structural properties, electronic properties, DOS and phonon properties.

The remaining part of the paper is organized in the following way. In Sec II, we discuss the computational details and the system under our study. Sec III gives a brief description of results of our work. Here, we present the analysis of total energy, band structure, density of states and phonon properties of rutile crystal of TiO_2. The last Sec IV summarizes the major findings and possible extensions of the ongoing research.

Materials and Methods

In the present work, we have incorporated Density Functional Theory (DFT) (Hohenberg 1964 and Kohn 1965) implemented in the Quantum Espresso (QE) (Giannozzi *et al*. 2009) code to study the structural properties of rutile crystal of TiO_2. The Perdew-Burke-Ernzerhof (PBE) (Perdew *et al*. 1996) form of generalized gradient approximation (GGA) was used for the exchange-correlation potentials. The fhi model of ultra-soft pseudo potential was used to account the interaction between the ion cores and valence electrons. The unit cell was optimized with respect to lattice parameters: (a) lattice constant 'a' and (b) ccut 'c/a'; kinetic energy cut-off (ecut) for plane wave and number of k-points along x, y and z- axes respectively. Based on convergence tests, we obtained the lattice constant 'a' for the unit cell of rutile crystal of TiO_2 as 8.61 Bohr (4.55 A^0) and c-cut 'c/a' as 0.64 which agrees quite well with the previous results (Landmann *et al*. 2012; Hameeuw *et al*. 2006).

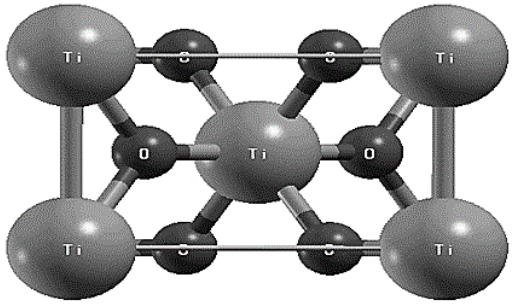

Figure 1. Rutile crystal of TiO_2 (Kokalj 2003).

The plot of the total energy versus the number of k-points reveals that the energy of the rutile crystal is almost constant after n_{kx} equal to 8. Hence a mesh of 8*8*12 k-points could be used for the Brilluoin zone integration. A plane wave basis set with energy cut-off value of 60 Ry (816 eV) for the wave-function is used for the expansion of the ground state electronic wave functions. The system was fully relaxed with the residual forces smaller than 0.001 eV/A^0. These ground state calculations were then used to compute the band structure 251 k-points were used in the summation over bands in the self-energy calculations and band calculations.

Results and Discussion

Electronic Structure Calculations

In order to study the electronic properties of rutile crystal of TiO_2, we have to study the band structure and density of states (DOS). We have studied the band structure calculations of rutile structure of TiO_2 by defining the high symmetry points (i.e Γ-X-R-Z-Γ-M-A-Z) on the edges of irreducible Brilluoin zone. We have taken 251 k-points along the specific direction of irreducible Brilluoin zone in order to obtain fine band structure. We have performed the band structure calculations along the path Γ-X-R-Z-Γ-M-A-Z in irreducible Brilluoin zone. Figure 2 shows the band structure of rutile crystal of TiO_2.

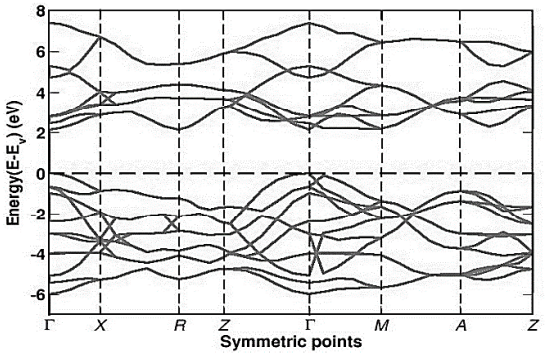

Figure 2. Band structure of rutile crystal of TiO_2.

From the band structure of the electron levels for rutile crystal of TiO_2, we have found that minimum of conduction band (CBM) and maximum of valence band (VBM) both lies at the same symmetrical k-point Γ. So, rutile crystal of TiO_2 is a direct band gap insulator located at Γ point of the Brilluoin zone with the band gap of 2.18 eV as shown by figure 2.

The band gap obtained from our present work 2.18 eV is somehow close to the reference band gap of 2.0 eV (Glassford and Chelikowsky 1992). However, the experimental value of band gap of rutile crystal of TiO_2 is found to be more than 3.0 eV (Cho *et al*. 2006; Landmann *et al*. 2012).

The obtained band gap is much smaller than the experimental value. This discrepancy is due to shortcoming of LDA. Therefore, other approximations have to be implied in order to obtain the direct band gap close to the experimental value. The approximation to be used may be LDA+U or GGA or perturbation theory. So the band structure calculation of rutile TiO_2 is quite exciting.

The density of states (DOS) is defined as the number of states per unit energy range available for the particles to be occupied. It indicates how densely packed quantum states in a particular system. It plays an important role in the calculation of various parameters that give the insight of the different electronic, magnetic and transport properties e.g. specific heat and paramagnetic susceptibility of a substance, mobility of charge carriers, diffusion properties (Kittel 2004). The total density of states for rutile crystal of TiO_2 is shown in the figure 3.

The dotted line indicates the position of the Fermi level which has been set equal to zero. The total DOS structure obtained in this work is comparable with the other research work (Cho *et al*. 2006; Landmann *et al*. 2012).

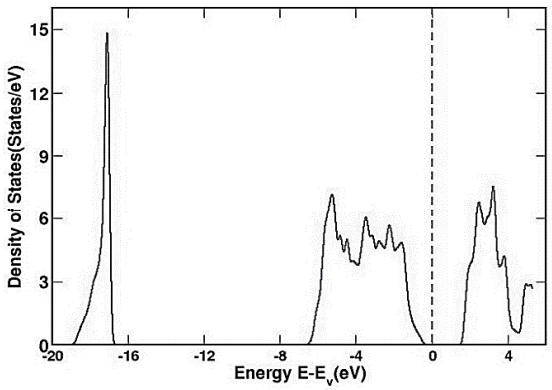

Figure 3. Total DOS of Rutile TiO_2.

The gap near the Fermi level shows that the rutile structure is a certain band gap insulator.

Figure 3 showed that the electrons are densely occupied to the left of Fermi level in comparison to that to the right of Femi level. We have also studied the projected electronic density of states for rutile TiO_2 which is shown in figure 4.

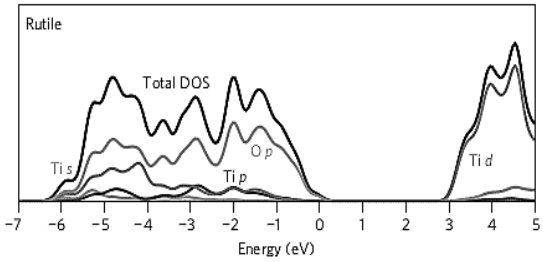

Figure 4. Projected DOS of rutile TiO_2.

From Figure 4, it is clear that the valence band edge is dominated by O-2p orbitals than O-2s orbitals. Ti-3s, Ti-3p and Ti-3d orbitals all contribute in the total density of states. But Ti-3d contributes more significantly than Ti-3s and Ti-3p orbitals. Therefore, the conduction band edge is dominated by Ti-3d orbitals than Ti-3s and Ti-3p orbitals.

The position of the conduction and valence bands of ionic material TiO_2 is determined by the electrostatic potential and the optical dielectric response (Scanlon *et al*. 2013). From the plot of projected density of states, we can conclude that the excess electrons will be occupied by 3d states of Titanium, whereas electron holes are occupied by 2p states of Oxygen.

For the comparative study of band structure and DOS, we have plotted the band structure and total DOS in the same graph.

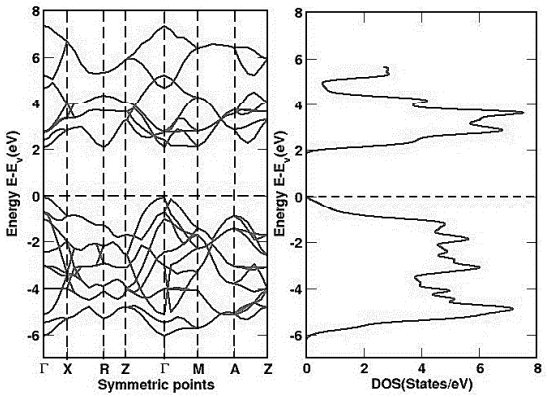

Figure 5. Band-DOS structure of rutile TiO_2.

From Figure 5, it is clear that the band structure and total DOS of rutile TiO_2 agrees quite well.

Phonon Properties

A phonon is a collective excitation in a periodic, elastic arrangement of atoms or molecules in condensed matter, like solids and some liquids. It plays a major role in the study of thermal properties like calculation of thermal conductivity, an-harmonic effect, susceptibility, heat capacity, etc.

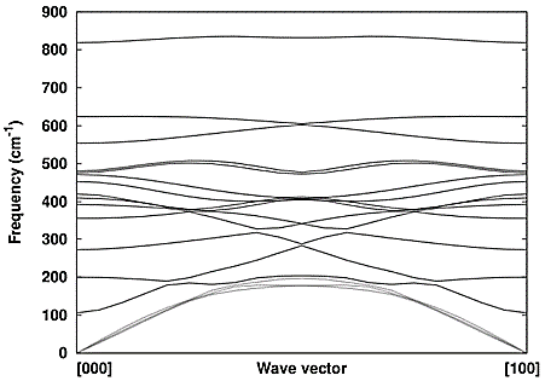

Figure 6. Phonon spectrum showing acoustic and optical modes of phonons for the orientation [1 0 0].

We have studied the phonon spectrum and phonon density of states of rutile TiO_2 using density functional perturbation theory (DFPT) (Baroni *et al*. 1987). We have calculated the phonon dispersion relation of frequency (ω) vs wave vector (k) graph for three different orientations in [1 0 0], [1 1 0] and [1 1 1] directions. The phonon spectrum of these three orientations are shown in following figures 6, 7, 8.

From the comparative study of phonon spectrum along three different orientations, we observed that the frequency gap in [1 0 0] orientation is higher than other two orientations.

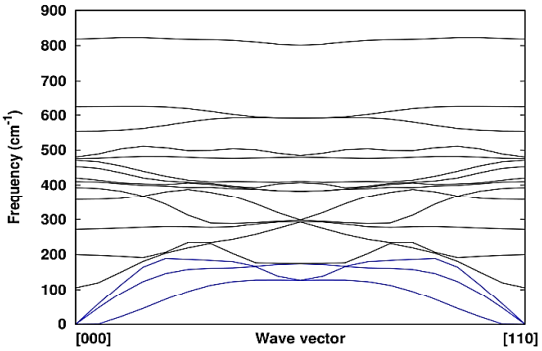

Figure 7. Phonon spectrum showing acoustic and optical modes of phonons for the orientation [1 1 0].

In figures 6, 7, 8 there are 3 acoustic phonons indicated by blue lines and 15 optical phonons represented by black lines.

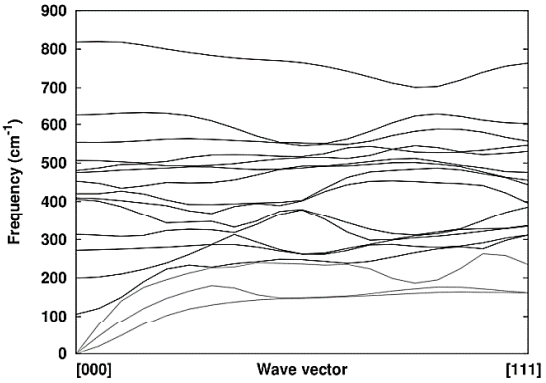

Figure 8. Phonon spectrum showing acoustic and optical modes of phonons for the orientation [1 1 1].

We have also calculated the phonon DOS for different k points grid 12*12*16, 16*16*24 and 24*24*32. Due to time efficiency and computational cost, we have calculated the phonon DOS for 12*12*16 grid as shown in figure 9.

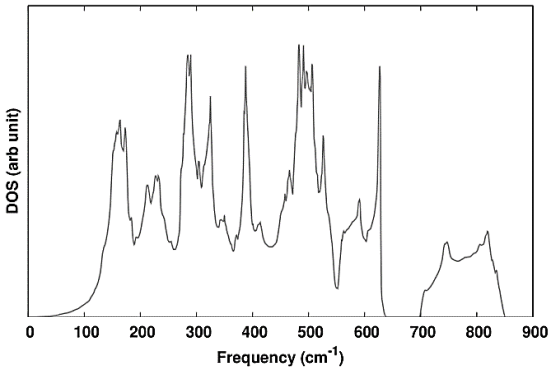

Figure 9. Phonon DOS of rutile TiO_2.

From dispersion curve, the branch corresponding to lower frequency is acoustic phonon and that corresponding to higher frequency is optical phonon. It is clear that the frequency is a periodic

function of wave vector k. Forbidden energy bang (gap) exists between the acoustic and optical phonons which cannot propagate. The width of forbidden gap increases as the ratio of masses (M_{Ti} / M_O) of TiO_2 increases.

Phonon DOS indicates how densely phonons are occupied in the given k-grid. From Figure 9, it is clear that the phonons are densely packed towards the left of frequency gap than that towards the right. There are sharp peaks between the frequency ranges of 300 to 650cm^{-1}. It illustrates that the phonons are compactly occupied in this frequency range.

Conclusion

We have studied a first-principles study of structural, electronic and phonon properties of rutile crystal of TiO_2. The band structure calculation shows the rutile TiO_2 is a direct band gap insulator with the band gap of 2.18 eV. The obtained band gap is very much less than the experimental value because of underestimating LDA approximation. The band gap can be made in close agreement with the experimental result by implying LDA+U, GGA or perturbation theory. We then analyzed the DOS which reveals that rutile TiO_2 is non-magnetic.

The electrons are densely occupied near to the left of Fermi level than the right of Fermi level. Finally we have studied the phonon properties of rutile crystal of TiO_2. The phonon spectrum of ω vs k along three different orientations [1 0 0], [1 1 0] and [1 1 1] shows the large frequency gap in [1 0 0] orientation. The sharp picks in the phonon DOS indicates the phonons are more densely occupied in the frequency range 300-650 cm^{-1}.

Acknowledgements

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