Electronic And Optical Properties Of Tib Compound: Ab Initio Simulations

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Abstract: We have investigated the electronic and optical properties of TiB monoboride using the density functional theory within the generalized gradient approximation (GGA) for exchange and correlation. Ground state properties such as lattice constant, cell volume and bulk modulus are calculated. The optimized lattice constant is in good agreement with the experimental and available theoretical results. The band structure and density of states (DOS) have been calculated along high symmetry directions in the first brillouin zone. The calculated band structure predicts that the TiB compound is metal. Further the features of optical properties such as reflectivity, absorption, refractive index, dielectric function, conductivity, loss function are obtained and discussed. All these calculations have been carried out using CASTEP computer code. This is the first theoretical prediction of these properties.

KEYWORDS: First principle calculations, monoboride, electronic properties, optical properties.

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1. Introduction

The transition metal borides, as one of the most important family of non oxide ceramics, and it have been attractive to research community due to their remarkable physical properties. The transition metals possess many attractive properties such as high strength [1,2], super hardness [3,4], high ferromagnetism [5], high melting point, superconductivity [6,7], and thermodynamic stability. The TiB monoboride plays an important role in different M-matrix alloys, especially in Ti matrix alloys [8-10]. The TiB compound is a NaCl-type face centered cubic (FCC) structure with Fm-3m space group has been reported [11-15]. A few numbers of theoretical and experimental works have been carried out of TiB monoboride. Let us note that the most of the works are investigated the structural, anisotropic elastic and thermodynamic properties. To the best of our knowledge, the electronic and optical properties of TiB monoboride with NaCl structure are still unexplored. The optical properties including dielectric function, refractive index, absorption coefficient, energy loss function, reflectivity and conductivity are very important in practical applications. In this paper, the structural, electronic and optical properties of TiB monoboride are investigated using first principle calculations. . First principles calculation offer one of the most powerful tools carrying out theoretical prediction of an important number of remarkable physical and chemical properties of materials with a great accuracy. The remaining parts of this paper are organized as follows: the computational method is described in section 2, the numerical results and discussion are given in section 3, and finally the conclusion is presented in section 4.

2. Computational method

The present calculations are performed with the ab initio method based on the density functional theory (DFT) [16] using the Cambridge Serial Total Energy Package (CASTEP) [17] code. The exchange correlation potentials are described by the generalized gradient approximation (GGA) in the scheme of Pedew-Burke-Eruzerhof (PBE) [18]. In the present calculation, the cut off energy of atomic wave functions was set to be 500 eV. We get a good convergence using a 6 × 6 × 6 set of Monkhorst – Pack mesh [19] grid for the total energy calculation. The optimizations of structural parameter were conducted by using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization [20]. Coulomb potential energy created by electron-ion interaction is described using the Vanderbilt – type ultrasoft pseudo potential [21] for all calculations except for the optical properties as Norm-conserving pseudo potential is used for the calculations. The orbital's of B ($2s2\ 2p^1$) and Ti ($3d^2\ 4s^2$) are treated as valence electrons. The setting about tolarances of the geometry optimization were set to 1.0×10^{-5} eV/atom for energy, 0.03 eV/Å for force,1×10^{-3} Å for ionic displacement, and 0.05 GPa for stress. These parameters are carefully tested and sufficient to lead to a well converged total energy.

3. Result and Discussion

3.1 Structural properties

The lattice constants and the atomic positions of TiB have been optimized as a function of the normal stress by minimizing the total energy. The TiB monoboride of NaCl-type possess a cubic structure with the space group Fm-3m (No. 221). It has a face centered cubic structure in which B atoms occupying the 4a site at origin while Ti atoms occupying the (½, ½, ½) positions. The optimized crystal structure of NaCl-type TiB monoborides are illustrates in Fig. 1.

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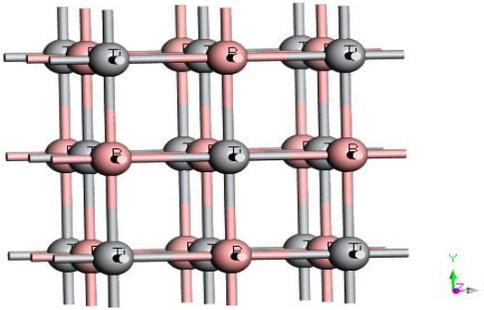
Fig. 1. Crystal Structure of the TiB monoboride

The calculated results of the structural parameters of TiB are presented in Table 1, along with the experimental and theoretical results. From Table 1, it can be seen that our calculated ground state lattice constants are very close to the both experimental [22] and available theoretical [23] values. The calculated lattice constant of our present work is 4.528 Å which exhibits 7 % deviation from the experimental values as shown in Table 1. The different calculation method and the different condition can be reason for this cxisting discrepancy. This ensures the reliability of the present DFT based first principles investigations.

Table 1. The calculated equilibrium lattice constant "a_0", unit cell volume "V_0" and bulk modulus "B_0" of TiB monoboride.

Properties	Expt.[22]	Other Calculation[23]	Present Calculation	Deviation from Expt. (%)
a_0 (Å)	4.202	4.528	4.528	7
V_0 (Å^3)	74.194	92.837	92.836	-
B_0 (GPa)	-	-	255.031	-

3.2 Electronic properties

The obtained electronic band structures of TiB monoboride using the generalized gradient approximation (GGA) along the high symmetry directions in the first Brillouin zone and are shown in Fig. 2. The data are presented in the energy range from -20 to 40 eV relative to the Fermi level. From Fig. 2, it is observed from the band structure, the TiB compound under study is metallic because a number of bands are overlapping at the Fermi level.
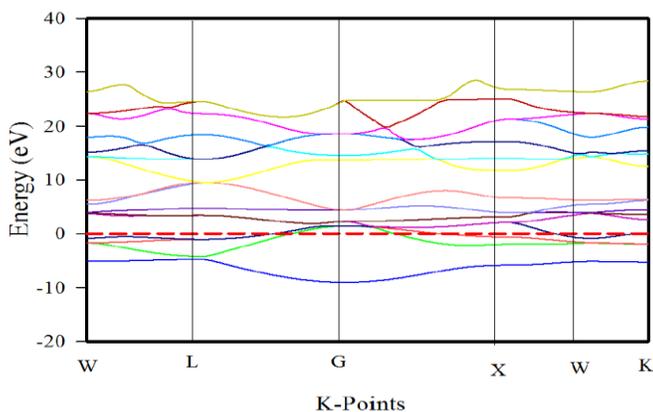

Fig. 2. The electronic band structure for TiB monoboride along several lines of high symmetry in the Brillouin zone.

The density of states (DOS) is an important role to describe the physical properties of materials [24]. The total density of states (TDOS) and partial density of states (PDOS) of TiB monoboride near the Fermi level are presented in Figure 3. Here, in this calculation, the Fermi level is set to 0 eV. We have treated Ti – 3d^{2}4s^2 and B – 2s^{2}2p^1 as valence electrons. It can be observed that the main bonding peaks locates in the energy range between the Fermi level and -5.0 eV, in which the most dominant contribution comes from the d states of the Ti atoms and a small amount of s, p orbital of B atoms. According to the PDOS and TDOS the lower valence band located at -9.0 eV to -5.0 eV is composed by Ti – 3d, Ti – 4s, B – 2p and B – 2s states and it is dominated by Ti – 3s and B – 2p states. The Ti – 3d states play the dominant role near Fermi level (E_F). These hybridizations imply that the interatomic forces are central in TiB compound which is also confirmed in Ref. [25]. To inspect the bonding property, we make further investigations on Mulliken overlap population [26] of TiB monoboride. Mulliken overlap population is a quanative criterion for assessing the covalent or ionic behavior of bonds. The atomic Mulliken population and bond population of TiB compound are presented in Table 2. A high value of the bond population indicates a covalent bond where as a low value indicates ionic bond proposed by Y. Cao et. al. [27]. The value of bond population is zero denotes the perfectly ionic bond and the values greater than zero indicates the increasing degree in covalency [28]. From Table 3, we have seen that the value of bond population is positive meaning that B-Ti bond exhibits covalent character.
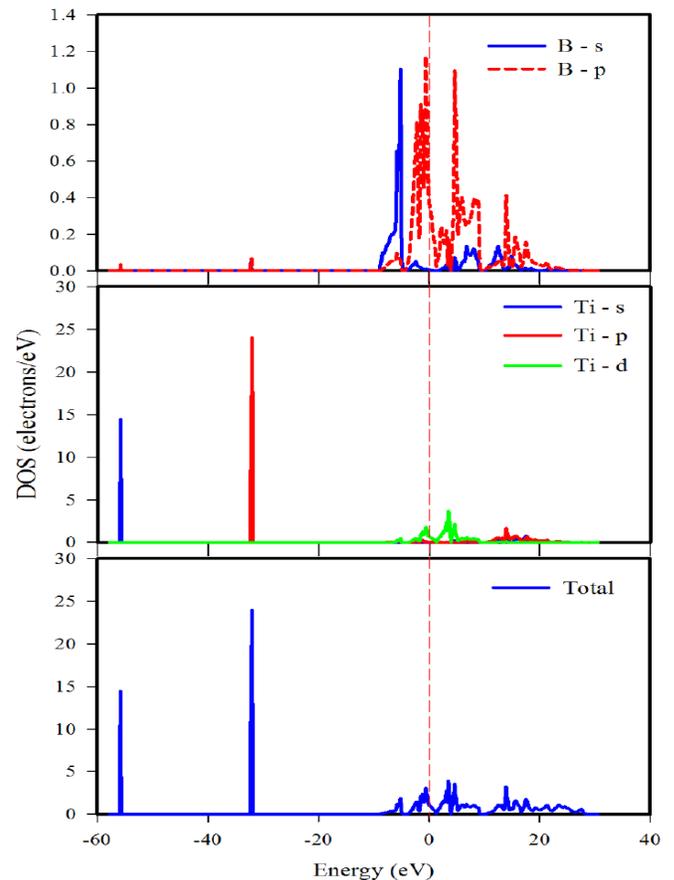

Fig. 3: Total density of states (TDOS) and partial density of states (PDOS) of TiB monoboride.

Table 2. Mulliken electronic populations of TiB monoboride.

Species	S	p	d	Total	Charge	Bond	Population	Lengths
B	1.25	2.34	0.00	3.59	-0.59	B1-Ti 1	1.82	2.264
Ti	2.08	6.62	2.71	11.41	0.59			

3.3 Optical properties

The details study of the optical function give a better understanding of the electronic properties of materials. The optical functions of a TiB compound can be obtained from the complex dielectric function, $\varepsilon (\omega) = \varepsilon_1 (\omega) + i\varepsilon_2 (\omega)$, where $\varepsilon_1(\omega)$ is the real part and part $\varepsilon_2(\omega)$ is the imaginary part. $\varepsilon_2(\omega)$ part is obtained from the momentum matrix between the occupied and the unoccupied electronic states and calculated directly using [29]:

$$\varepsilon_2(\omega) = \frac{2e^2\pi}{\Omega\varepsilon_0} \sum_{k,v,c} \left|\psi_k^c\right| u.r \left|\psi_k^v\right|^2 \delta\left(E_k^c - E_k^v - E\right)$$

Where u is defined as the polarization vector of the incident electric field, ω is the frequency of light, e is the electronic charge, ψ_k^c is the conduction band wave function and ψ_k^v is the valence band wave function at k respectively. The optical functions such as refractive index, loss function, absorption spectrum, conductivity and reflectivity are obtained by using Eqs. 49 to 54 in ref. [29]. The optical properties of TiB compounds under study are calculated for photon energies up to 80 eV for polarization vector [100]. We have used a 0.5 eV Gaussian smearing for all calculations.
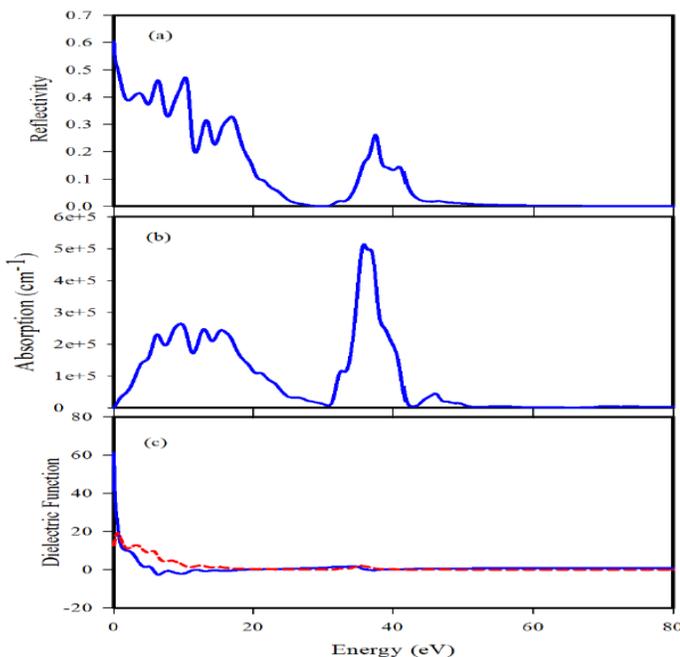

Fig. 4. The reflectivity, absorption and dielectric function of TiB compound for polarization vector [100].

Figure 4(a) illustrates the reflectivity spectra of TiB monoboride

as a function of photon energy. It is found that the reflectivity is 0.50-0.60 in the infrared region and the value drop in the high energy region with some peaks as a result of intraband transition. It is also found that the reflectivity in TiB is high in visible and ultraviolet up to 16 eV regions indicating the alloy as a promising candidate for use as a coating material to avoid solar heating. Figure 4(b) shows the absorption coefficient of TiB compound as a function of photon energy. It provides data about solar energy conversion efficiency and indicates how far light of energy (frequency) can penetrate into the material before being. The absorption coefficient indicates that of TiB compound under study reveals metallic character since the spectra starts from 0 eV.
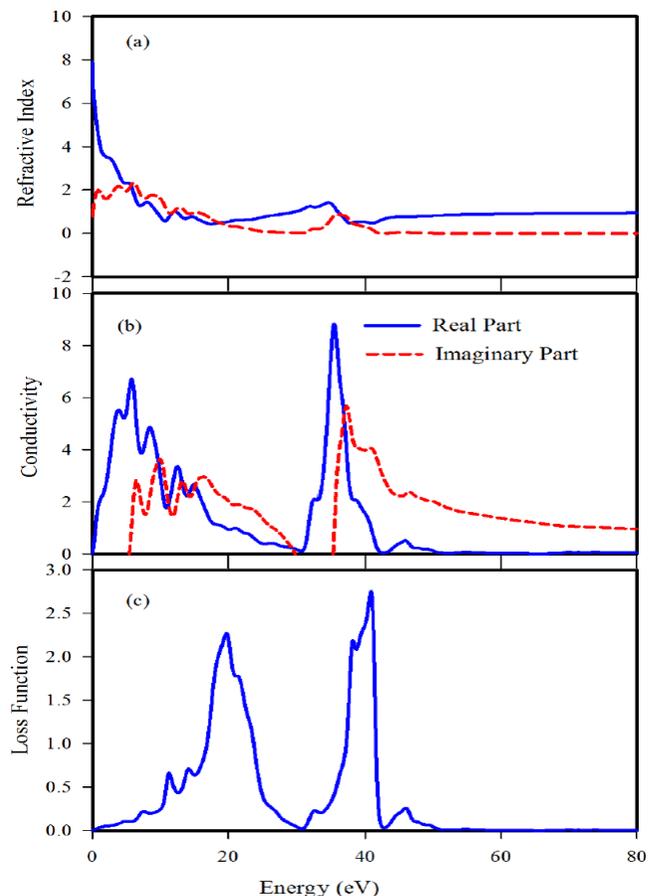

Fig. 5. The refractive index, conductivity and loss function of TiB for polarization vector [100].

The refractive index is an important optical properties of a material to which determine how much light is refracted when entering a material. Figure 5(a) shows the refractive index of TiB compound. From Figure 5(a), we obtained the value of static refractive index is 8 for TiB compound. The refractive index of TiB compound is higher in the low energy region and gradually decreased in the high energy region. The loss function is an important optical parameter to describe the energy loss of a fast electron traversing materials [30]. In Figure 5(c) shows the energy loss function as a function of photon energy. The highest peaks are found 41eV for TiB compound. Figure 5(b) illustrates the conductivity spectra of TiB compound as a function of photon energy. From Figure 5(b), it is found that the photoconductivity of these material starts with zero photon energy meaning the material under

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study have zero band gap. Several maxima and minima are observed in the conductivity plot. Moreover, electrical conductivity of these compound increases as a result of absorbing photons [31]. The imaginary and real parts of the dielectric function are displayed in Fig. 4(c). The real part of the dielectric function to explain about the polarization of material due the applied electric field. The imaginary part is related to the absorption in a material. In Fig. 4(c), we obtain the value of real part becomes zero at about 5 eV for TiB compound. The value of $\varepsilon_2(\omega)$ becomes non zero, then absorption begins. Materials with high dielectric constants are useful for manufacturing of high value capacitors.

4. Conclusion

In these work, first principles calculations based on density functional theory have been used to investigate the structural, electronic and optical properties of TiB compound. The structural properties including lattice parameter, cell volume and bulk modulus were calculated successfully. The calculated lattice parameters are in good agreement with the available experimental and theoretical results. For the first time we have used GGA-PBE to calculate the band structure of TiB compound and analyzed. We have also investigated the PDOS and TDOS of TiB compound and analyzing these diagrams it is concluded that the interatomic forces are central in TiB compound. The result of DOS indicating that the TiB compound exhibit metallic nature. We have also investigated the Mulliken overlap population indicates that the covalent nature is dominant in TiB compound. For the first time we have studied the optical properties such as reflectivity, refractive index, energy loss spectrum, conductivity, absorption and dielectric function of TiB material.

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