

Theoretical prediction of the structural, electronic and optical properties of HfB monoboride from first principle calculations

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Abstract : *The structural, electronic and optical properties of HfB monoboride have been investigated using first principles calculations within the framework of density functional theory and the Pseudopotential approximation. The calculated lattice parameters were in good agreement with the experimental and available theoretical data. The electronic and bonding properties of HfB monoboride are analyzed using band structure, DOS and Fermi surface. The d-states of Hf atoms play an essential role in differentiating the bonding behavior of this compound. Further the features of optical functions (reflectivity, absorption, refractive index, dielectric function, conductivity, loss function) are obtained for the first time and discussed. All these calculations have been carried out using CASTEP computer code.*

KEYWORDS: Density functional theory, electronic properties, Fermi surface, optical properties.

1. Introduction

The transition metal borides have always been of strong interest among the research community due to their prominent applications. The transition metal borides possess many advantages such as the high melting point, high strength [1, 2], super hardness [3, 4], superconductivity [5, 6], high ferromagnetism [7], thermodynamic stability and resistance to attack by molten metal and glass. As a kind of the transition metal boride, HfB monoboride play a vital role in various alloys, especially in Ti matrix alloys [8-10]. The crystal structure of HfB monoboride is formed in the primary crystallization reaction from the amorphous phase, strong interest have been paid to the mechanism of the nanocrystalline structure evolution in these alloys [11]. The remarkable physical properties of HfB monoboride have been investigated extensively in recent years. A number of theoretical and experimental works have been carried out on the structural, elastic properties of HfB compound. Recently, Bo Huang et al. [12] have been investigated the structural, anisotropic elastic and thermal properties of MB (M = Ti, Zr and Hf) monoborides. The elastic properties and formation enthalpy of TiB have been calculated by K.B. Panda et al. [9]. X. W. Xu et al. [13] have performed a density functional study on the elastic properties and chemical bonding by using the first principle calculations. The systematic information of mechanical properties in the HfB monoboride hinders the better understandings and applications of this transition-metal boride. To the best of our knowledge, there are no reports on the study of structural, electronic and optical properties of HfB material.

The present work aims to investigate the structural, electronic and optical properties of HfB monoboride using the first principles calculations. The rest of this paper is organized as follows: Section 2 is devoted to the description of our methods of calculation. In section 3 the results and discussions are presented. Finally, in section 4 the conclusions of the present work are given.

2. Computational method

The present calculations have been performed by using the plane-wave pseudo potential method as implemented in the CASTEP code [14], based on the density functional theory (DFT) [15]. The generalized gradient approximation (GGA), in the scheme of Perdew, Burke and Ernzerhof (PBE) are made for electronic exchange-correlation potential energy [16]. Coulomb potential energy created by electron-ion interaction is described using the Vanderbilt –type ultrasoft pseudo potential [18] for all calculations except for the optical properties as Norm-conserving pseudo potential is used for the calculations. The orbital's of B ($2s^2 2p^1$) and Hf ($5d^2 6s^1$), are treated as valence electrons. The plane-wave cut-off energy was set to be 500 eV and the Brillouin zone sampling was carried out using the $6 \times 6 \times 6$ set of Monkhorst – Pack mesh [17].

The structural parameters of HfB monoboride were conducted by using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization technique [19]. In the structural optimization process, criteria of convergence 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 parameters and the atomic positions of HfB have been optimized as a function of the normal stress by minimizing the total energy. The HfB monoboride compound of NsCl-type structure with the space group Fm- $3m$. It has a face centered cubic structure in which B atoms occupying the 4a site at origin while Hf atoms occupying the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ positions. The optimized crystal structure of NsCl-type monoborides are illustrates in Fig. 1.

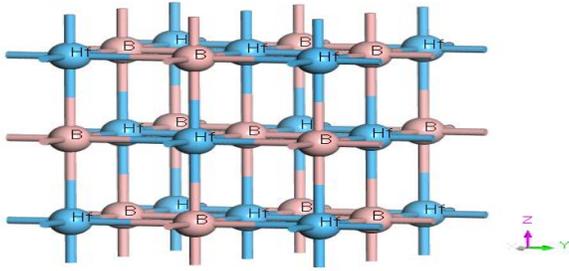


Fig. 1. Crystal Structure of the HfB monoborides

The calculated results of the structural parameters of HfB are listed in Table 1, along with the experimental and theoretical results. From Table 1, it can be seen that our calculated results agrees reasonably with other experimental [20] and theoretical results [12]. The calculated lattice constant of this present work is 4.855 Å. This ensures the reliability of the present DFT based first principles calculations.

Table 1. The calculated equilibrium Lattice constant “ a_0 ”, unit cell volume “ V_0 ” and bulk modulus “ B_0 ” of HfB monoboride.

Properties	Expt.[20]	Other Calculation[12]	Present Calculation	Deviation from Expt. (%)
a_0 (Å)	4.620	4.850	4.855	0.05
V_0 (Å ³)	98.61	114.43	114.43	-
B_0 (GPa)	-	-	269.30	-

3.2 Electronic properties

The electronic band structures of HfB monoboride are obtained using the generalized gradient approximation (GGA) along the high symmetry lines of the first Brillouin zone and are shown in Fig. 2. The data are presented in the energy range from -20 to 30 eV relative to the Fermi level. From Fig. 2, we can also find that the overlap between the conduction band and the valance band makes HfB exhibits metallic behavior.

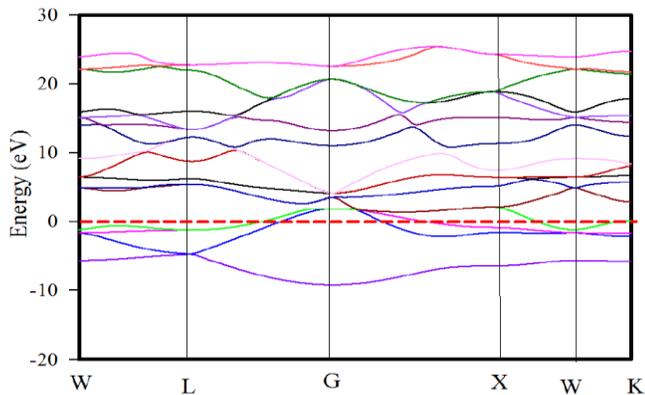


Fig. 2. The electronic band structure for HfB monoboride along several lines of high symmetry in the Brillouin zone

The density of states (DOS) of a system describes the number of states at each energy level which is available in the condensed matter physics. The DOS is an important parameter for understanding the bonding in a compound [21]. The total density of states (TDOS) and partial density of states (PDOS) for HfB compound near the Fermi level is presented in Fig. 3. Here we have treated Hf – 5d²6s² and B – 2s²2p¹ as valence electrons. In this calculation, the Fermi level (E_F) is set to 0 eV. It can be observed that the main bonding peaks locates in the energy range between the Fermi level and -6.0 eV, in which the most dominant contribution comes from the d states of the Hf 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 Hf – 5d, Hf – 6s, B – 2p and B – 2s states and it is dominated by Hf – 6s and B – 2p states. The Hf – 5d states play the dominant role near Fermi level (E_F). These hybridizations imply that the interatomic forces are central in HfB compound which is also confirmed in Ref. [22].

To inspect the bonding property, we make further investigations on Mulliken overlap population [23] of HfB compound. Mulliken overlap population is a quantative criterion for assessing the covalent or ionic behavior of bonds. The atomic Mulliken population and bond population of HfB compound are listed in Table 3. Y. Cao et al. [24] proposed that the low value of bond population indicates a ionic bond whereas a high value denote covalent bonds. The value of bond population is zero denotes the perfectly ionic bond and the values greater than zero indicates the increasing degree in covalency [25]. From Table 2, it can be seen that the value of bond population is positive meaning that B-Hf bond exhibits covalent character.

Table 2. Mulliken electronic populations of HfB monoboride.

Species	S	p	D	Total	Charge	Bond	Population	Lengths
B	1.3 5	2.4 5	0.0 0	3.80	-0.80	B-Hf	2.33	2.42 7
Hf	0.3 7	- 0.0 3	2.8 6	3.20	0.80			

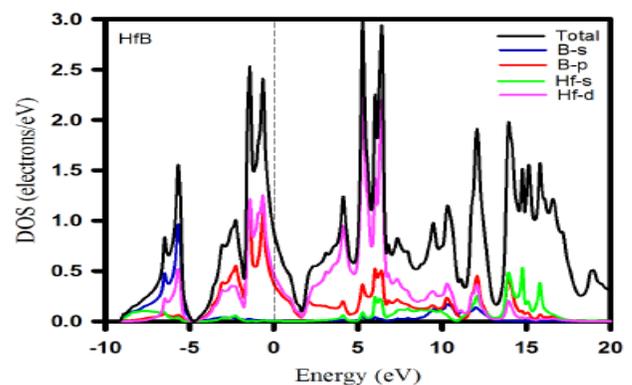


Fig. 3: Total density of states (TDOS) and partial density of states (PDOS) of HfB monoboride.

3.3 Optical properties

The analysis of the optical functions of materials gives a better understanding of the electronic structure. The imaginary part of complex dielectric function, $(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, is obtained from the momentum matrix elements between the filled and unfilled electronic states and calculated directly using the equation [26] -

$$\epsilon_2(\omega) = \frac{2e^2\pi}{\Omega\epsilon_0} \sum_{k,v,c} |\psi_k^c| u \cdot r |\psi_k^v|^2 \delta(E_k^c - E_k^v - E)$$

Where, ψ_k^c is the conduction band wave function and ψ_k^v is the valence band wave function at k respectively, u is the vector defining the polarization of the incident electric field, ω is the light frequency, e is the electronic charge. Using the Kramers-Kronig transform, the real part is derived from the imaginary part $\epsilon_2(\omega)$. All other optical functions such as refractive index, absorption spectrum, loss function, reflectivity and conductivity are those given by equation 49 to 54 in ref. [26]. Fig. 3 and Fig. 4 displayed the optical functions of HfB calculated for photon energies up to 40 eV. We have used a 0.5 eV Gaussian smearing for all these calculations. This smears out the Fermi level, so that k-points will be more effective on the Fermi surface.

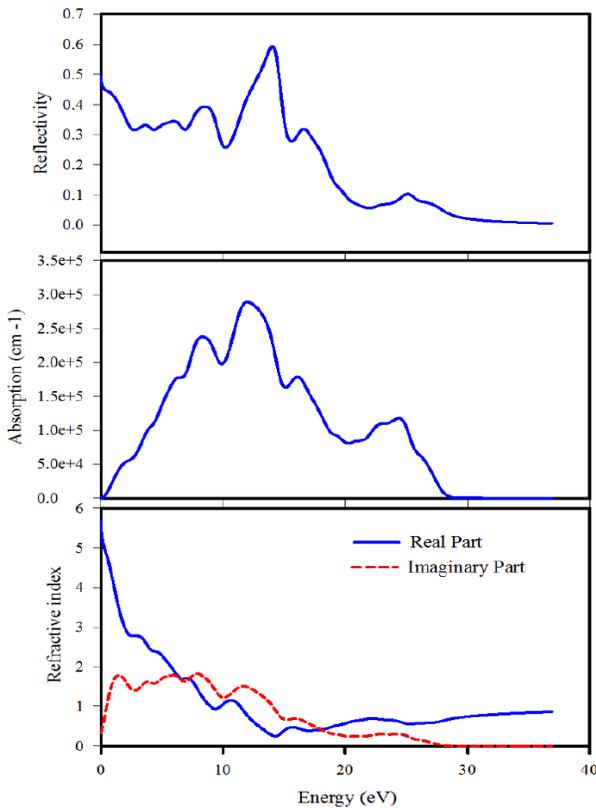


Fig. 3. The reflectivity, absorption and refractive index of HfB monoboride for polarization vector [100].

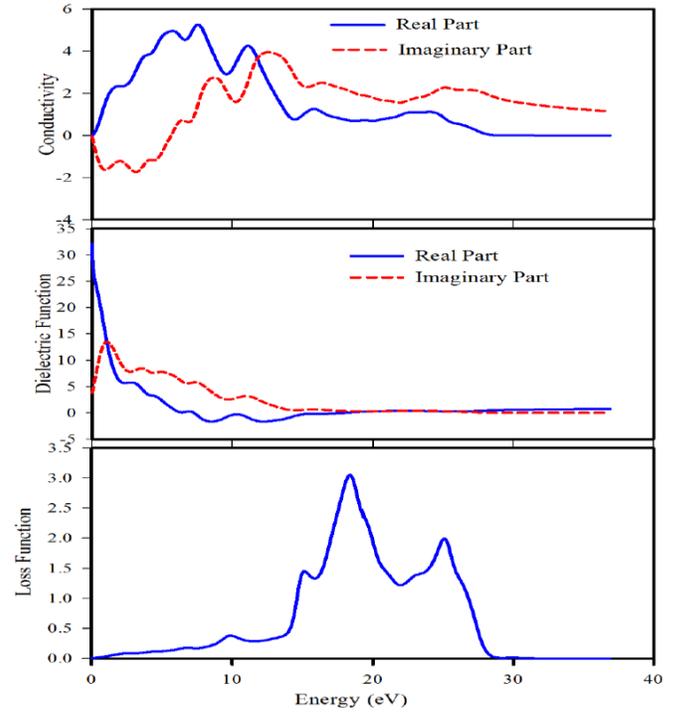


Fig. 4. The conductivity, dielectric function and loss function of HfB for polarization vector [100].

The reflectivity spectra as a function of photon energy as shown in Fig. 3. The reflectivity spectra of HfB, shows promise as good coating materials between 10 eV and 15.5 eV regions. The HfB materials has no band gap as evident from band structure, the photoconductivity starts with 0 eV photon energy as shown in Fig. 4. As shown in Fig. 4, the photoconductivity and hence electrical conductivity of the materials increases as a result of absorbing photons.

The absorption coefficient provides data about optimum solar energy conversion efficiency and it indicates how for light of a specific energy can penetrate into the material before being absorbed. The absorption spectra as shown in Fig. 3 exhibit the metallic nature, since the spectra starts from 0 eV photon energy.

The real and imaginary parts of the dielectric function are displayed in Fig. 4. In Fig. 4, the electron energy loss functions describing the energy loss of a fast electron traversing a material equally large at the plasma frequency [27]. Prominent peaks are found at 13 eV and 28 eV, which indicate rapid reduction in the reflectance.

4. Conclusion

We have investigated the structural, electronic and optical properties of HfB monoboride by performing the generalized gradient approximation (GGA) within the framework of density functional theory. The calculated lattice parameters are in good agreement with the experimental and theoretical data. Band structure and total densities of states analysis suggest that HfB

material exhibit metallic behaviour. The investigation of DOS shows that the major contribution near the Fermi level comes from Hf-d states. We have also investigated the Mulliken overlap population indicates that the covalent nature is dominant in HfB 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 HfB material. From an analysis of optical functions, it is found that HfB is a good dielectric material. Further the reflectivity is seen to be high in visible – ultraviolet regions between 10 eV to 15 eV for HfB showing promise as good coating materials.

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