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Ab initio study of the thermodynamic, electronic and optical properties of WC (B_h) phase ZnO under pressure

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ARTICLE INFO	A B S T R A C T
<i>Keywords:</i> WC phase ZnO First principles Electronic and optical properties B3LYP	The present investigation highlights the structural, thermodynamic, electronic, and optical properties of WC (B _h) phase ZnO calculated by means of first principles and Debye model approach. Acquired results revealed that pressure-induced phase transitions followed the sequence (B4 \rightarrow WC \rightarrow B2). The trend of thermodynamic properties with temperature and pressure has been discussed. Hybrid Functional (B3LYP) was employed to explore the bands and optical properties. The band gap under pressure is fitted well by a quadratic equation. Calculations demonstrate that an increase in band gap with increasing pressure leads to a blue shift in optical properties. The calculated band gap validates that the WC phase is an insulator, whereas the negative real part of dielectric function $\varepsilon_1(\omega)$ indicates that it possesses metallic behaviour at around 21.9 & 23.5 eV. The relation

WC phase ZnO for technological applications.

1. Introduction

ZnO is a renowned promising semiconductor with excellent optical properties, wider band gap, and high excitation binding energy. It is also an important mineral found in the earth's lower mantle [1-4]. The wurtzite (B4) phase is considered the most stable phase of ZnO at normal temperature and pressure. It transforms into multiple phases with unique properties under varying pressure. Recently, ZnO has become the most necessitated choice of researchers by virtue of its widespread applications in the electronics & energy industrial sectors [5–10]. It is used in developing photo resistors [11], magnetic semiconductors [12], thinfilm transistors [13], heterojunction devices [14], bio and gas sensors [15,16]. The behaviour and promising properties of ZnO under pressure are the hot topics of contemporary research. Consequently, plenty of experimental and theoretical research has been conducted to explore the phase transitions by modern computational techniques and highpressure equipment technology [17,18]. The literature survey has declared that experimental and theoretical calculations prove the transitions from wurtzite (B4) to B1 (NaCl), B2 & B3 phases of ZnO [19-26].

Recently different researchers, by using the simulated approach and Ab-initio calculations, proposed intermediate (GeP, NiAs, PbO) phases in the ZnO system [27,28]. Molepo and Joubert predicted WC (B_h) type

modification at high pressure in the B4 \rightarrow B2 transition path [29]. The thermodynamic properties are important for the geoscience processes [30]. Moreover, studying the thermodynamic and optical properties of ZnO under high pressure is expedient for identifying the phase structure of ZnO under extreme pressure [23,31]. The relations between optical properties and pressure can be used to determine the pressure and geoscience processes. It has been continuing focus research due to its significance and applications in material sciences, geoscience, and optics. However, the properties of the proposed potential WC phase ZnO have not been investigated yet. Therefore, conducting a pressure-induced study is an imperative aspect for the future applications of ZnO. Although experimental studies are in exercise, the first principles method based on density functional theory (DFT) is also an effective way to explore the thermodynamic, optical, and electronic properties of materials under various pressures [32–37].

between absorption constant and pressure is examined in detail. This exploration demonstrates the potential of

The electronic band gap of materials is an important property. Standard first principles method with LDA or GGA is not supposed to be much successful in computing the reliable band gap of ZnO. Luckily the hybrid functional B3LYP method is found to be much efficient in calculating accurate band gap and optical properties [38–41]. By keeping in view of the above rationale, we present a profound study of the electronic & optical properties of WC phase ZnO under pressure. It is

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Received 11 August 2020; Received in revised form 16 November 2020; Accepted 7 December 2020 Available online 15 December 2020 0921-5107/© 2020 Elsevier B.V. All rights reserved. found that the B4 phase ZnO is transformed to the WC phase, and the WC phase is transformed to the B2 phase with increasing pressure. First principles with LDA were used to get transition points, and a Debye model was used to calculate the thermodynamic properties. A hybrid functional (B3LYP) is applied to calculate electronic as well as optical properties of ZnO in the WC phase. Optical constants are discussed in detail to give a deep insight into the effects of pressure change.

Our conducted research gives an extensive understanding of the behaviour of WC phase ZnO under pressure. Furthermore, some mineral inclusions from the earth's mantle contain ZnO, which provides information about the pressure in the process of mineral formation [42]. Based on our study, the formation pressure can be determined. Moreover, ZnO also can be used as a nanolaser in the chips tailored by pressure [43]. Hence, the Present investigation will boost the ongoing interest in the research of pressure-induced phases of ZnO for future mineral pressure determination and nanolaser applications.

2. Computational details

The Present calculations were performed by density functional theory (DFT) based Cambridge Sequential Total Energy Package (CASTEP) program, which is inbuilt in materials studio software [44,45]. The DFT method has proven to be one of the most accurate methods for the computation of the electronic structure of solids [46–52]. The standard local density approximation (LDA) method was used for geometry optimization as well as to calculate enthalpies for finding transition pressure. LDA method has been used frequently in calculations. It somewhat underestimates the lattice parameter and overestimates the bulk modulus. However, in the ZnO system, the LDA slightly underestimates the lattice parameter and better fits with the bulk modulus [53]. Therefore, the LDA method is applied in our calculations of the ZnO system. The cutoff energy of 571.4 eV, the monkhorst–pack *k* points of $5 \times 5 \times 4$ (B4) and $6 \times 6 \times 6$ (WC and B2) phase ZnO are used for sampling of the first Brillouin zone. The used electronic configuration of Zn and O atoms was $3d^{10}4s^2$ and $2s^22p^4$. The convergence energy, maximum force, displacement, and stress were fixed to 0.001 eV/atom, 100 eV/Å, 100 Å, and 100 GPa, respectively. Ultrasoft pseudopotentials [54], spin polarization, and Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [55] were also used with LDA to deal with the electron–electron interactions. The energy versus volume curve at different cell volumes is also calculated by using the LDA method.

After geometry optimization, thermodynamic properties were calculated by using the Debye model of heat. Becke's 3 parameter functional combined with Lee, Yang and Parr's correlation functional (B3LYP) along with norm-conserving pseudopotentials were availed to determine the electronic and optical properties under different pressure. We used the exchange–correlation (XC) functional parameter for the accurate estimation of the band gap. The used exchange-correlated parameter in B3LYP is 0.4; it can guarantee the calculated gap value of the ZnO is 3.44 eV, which matches with the experimental results (3.44 eV) [61]. In the calculations, we also used the fine cutoff energy of 1143.0 eV and monkhorst–pack *k* points of $4 \times 4 \times 2$ (B4), $4 \times 4 \times 4$ (WC and B2) phase ZnO. The calculations were taken in reciprocal space.

3. Results and discussion

3.1. Structural properties and phase transitions

Structural, electronic, and optical properties of materials are correlated to each other. Fig. 1 shows the crystal structures of B4, WC, and B2 phases of ZnO. Consequently, following the structural optimization, their properties were calculated. We determined the enthalpy (*H*) values of B4, WC as well as B2 phases under pressure range 0–200 GPa, calculated enthalpies were used to evaluate the phase transition points. Fig. 2 shows that the transitions of the B4 phase to the WC phase, as well as the WC phase to the B2 phase, take place at 30.1 GPa & 157.8 GPa,



Fig. 1. The crystal structures of B4 (a), WC (b) and B2 (c) phases after optimization at 0 GPa. The red color balls specify oxygen atoms and the gray color balls denote zinc atoms in the crystal. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. The calculated enthalpies of B4, WC and B2 phase ZnO as a function of varying pressure. The transition from B4 to WC and WC to the B2 phase is shown. The inset graph displays the enlarged view of B4 to WC transition and other inset ΔE graph shows energy difference in WC and B2 phase ($\Delta E = E_{B2}-E_{WC}$).

respectively. The acquired results are significantly in accordance to previously reported predicted values. In addition, the enthalpy (*H*) of phases increases by increasing the pressure and is found to be equal in value at transition points. The inset of Fig. 2 demonstrates the magnified view of B4 to the WC phase transition and the WC to B2 phase transitions with enthalpy difference ΔE ($\Delta E = E_{B2} - E_{WC}$).

While on the other hand, the structural properties of phases were also calculated. Table 1 shows the comparative analysis between the present and previously published experimental and theoretical results. The results shows that, @ 0 GPa, the lattice constants, bond angles & bond length of the WC phase were found a = b = 2.855 Å c = 2.620 Å, $\alpha = \beta = 90^{\circ} \gamma = 120^{\circ}$, and 2.105 Å, respectively. The calculated results declared that by increasing the pressure, bond angles of the WC phase does not change, whereas the lattice constants and bond lengths decrease continuously. Results indicate that @ 30.1 & 157.8 GPa the lattice constants decrease remarkably to a = b = 2.738 Å, c = 2.549 Å & a = b = 2.484 Å, c = 2.444 Å, respectively. Since the bond length also decreases,

Table 1

The calculated lattice parameters, bond length and volume results of B4, WC and B2 phase at 0 GPa and transition pressures. The present results are compared with previous theoretical and experimental data.

Pressure (GPa)	Phase	Reference	a = b (Å)	c (Å)	Bond Length (Å)	Volume (Å ³)
0	B4	Exp ^a	3.249	5.206		23.81
		Exp ^b	3.249	5.204		23.79
		Theory ^c	3.2562	5.2563	1.99	
		Theory ^d	3.19	5.18		
		Theory ^e	3.209	5.128		22.80
		Present	3.142	5.03	1.9	21.51
	WC	Theory ^d	2.89	2.64		
		Theory ^e	2.943	2.549		19.1
		Present	2.855	2.62	2.1	18.49
	B2	Theory ^d	2.61	2.61		
		Theory ^e	2.618	2.618		17.94
		Present	2.552	2.552	2.21	16.63
30.1	B4	Present	3.041	4.865	1.84	19.49
	WC	Present	2.738	2.549	2.03	16.54
157.8	WC	Present	2.484	2.444	1.88	13.06
	B2	Present	2.319	2.319	2	12.48

^a Ref. [20].

^c Ref. [23].

^d Ref. [28].

^e Ref. [29].

i.e., 2.030 Å & 1.884 Å, consequently, the decrease in bond length leads to the escalating Zn-O bond hybridization. On the basis of results represent in Fig. 2, it is assumed that as compared to the other phases, the B4 phase is found to be more stable with a relatively low enthalpy (*H*) value.

3.2. Thermodynamic properties

The thermodynamic properties are calculated by the Debye model. We used the Vinet equation of state (EOS) [56,57] to get the isothermal bulk modulus (B(T)). Eqs. (1)–(7) were used to calculate the heat capacity $C_{\rm p}$, thermal expansion coefficient (a(T)), and Helmholtz free energy. Since the melting point of B4 phase, ZnO is about 2248 K [58], the temperature used in our calculations is between 0 and 2000 K. The applied pressure values are the 0 GPa, transition pressure, and middle pressure.

$$\alpha(T) = \frac{1}{V(T)} \frac{\partial V(T)}{\partial T}$$
(1)

$$C_{V} = 3nk \left[4D\left(\frac{\Theta}{T}\right) - \frac{3\Theta/T}{exp(\Theta/T) - 1} \right]$$
⁽²⁾

$$C_p = C_v + \alpha^2 B V T \tag{3}$$

The *D* and Θ are Debye integral and temperature (Eq. (2)). We can calculate the Θ and *D* by Eq. (4) and (5).

$$\Theta = \frac{h}{k_B} \left[6\pi^2 V_2^{\frac{1}{2}} n \right]^{\frac{1}{3}} f(\nu) \sqrt{\frac{B}{M}}$$
(4)

We used Eq. (6) to get $f(\nu)$ from Poisson's ratio ν . The free energy is calculated by Eq. (7).

$$D(y) = \frac{3}{y^3} \int_0^y \frac{x^3}{e^x - 1} dx$$
(5)

$$f(\nu) = \left\{ 3\left[2\left(\frac{2}{3}\frac{1+\nu}{1-2\nu}\right)^{\frac{3}{2}} + \left(\frac{1}{3}\frac{1+\nu}{1-\nu}\right)^{3/2}\right]^{-1} \right\}^{1/3}$$
(6)

$$E(V) = E_0 - 2B_0 V_0 e^{-3/2 \left(\left(\frac{V}{V_0}\right)^{1/3} - 1 \right)} \frac{3 \left(\frac{V}{V_0}\right)^{\frac{1}{3}} B_0' - 3 \left(\frac{V}{V_0}\right)^{\frac{1}{3}} B_0' - 3B_0' + 5}{\left(B_0' - 1\right)^2} + \frac{4B_0 V_0}{\left(B_0' - 1\right)^2}$$
(7)

We first calculated the energy versus volume graph, which is plotted in Fig. 3a. The graph shows that the B4, WC, and B2 phases of ZnO possess low energy values at their equilibrium states. It is found that the B4 phase with the lowest energy value is comparatively more stable. The intersection points indicate that the energy and volume values of phases are equal at these points, as well as the phase transition begins afterward. The order of minimum equilibrium energy is B4, WC, and B2 phase, which means the phase transition order is B4-WC-B2. The transition order is in line with the order from enthalpy. We also calculated the bulk modulus, thermal expansion coefficient, and heat capacity under 0, transition, and middle pressure. In Fig. 3, we plotted the corresponding data of the B4 phase from the research of Seko et al. [59] and Wu et al. [60]. Fig. 3b, c, and d show that our thermodynamic results agree well with the other results [59,60]. Fig. 3b shows the calculated bulk modulus, which expresses that the modulus gently decreases with the increasing temperature of ZnO. Our calculated result for bulk modulus is in line with the report [53].

The calculated values of bulk modulus are also in line with the bulk modulus obtained directly from the minimization. The bulk modulus of B4 phase ZnO from minimization is 162.6 and 304.3 GPa at 0 and 30.1 GPa, respectively. For those obtained from the thermodynamic

^b Ref. [22].



Fig. 3. (a) Energy versus volume *E*(*V*) graph for B4, WC & B2 phases of ZnO calculated at different fixed volumes. The calculated bulk modulus (b), thermal expansion coefficient (c) and heat capacity (d) and free energy (e) of B4, WC & B2 phases of ZnO under corresponding pressure.

calculation, the bulk modulus of B4 phase ZnO is 170.9 and 312.2 GPa at 0 and 30.1 GPa, respectively. On the other hand, the bulk modulus of WC phase ZnO calculated from minimization is 305.4, 485.4, 642.8, and 792.6 at 30.1, 70, 110, and 157.8 GPa, respectively. For those obtained from the thermodynamic calculation, the bulk modulus values of WC phase ZnO are 318.1, 492.7, 653.1, and 804.9 at 30.1, 70, 110, and 157.8 GPa, respectively. The bulk modulus of the B2 phase calculated at 157.8 GPa directly from minimization is 804.2 GPa, while the thermodynamic estimation result is 818.5 GPa. Consequently, these two methods have reported similar results. For B4 and WC phases, the bulk modulus increases with increasing pressure at the same temperature.

Comparatively, the pressure has more effects on modulus than temperature. The B4 phase has the lower bulk modulus, while the B2 phase has a higher modulus. A higher modulus means that the structure is difficult to compress than the lower modulus. At the transition pressure, the calculated bulk modulus of the second phase is slightly higher than that of the first phase.

Fig. 3c shows that the thermal expansion coefficient increases with increasing temperature and decreases with increasing pressure. The coefficient increases rapidly below 500 K and gently increases after 500 K. At transition pressure, the expansion coefficient of second phase is higher than the first phase. Fig. 3d shows that the heat capacity increases

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rapidly below 400 K and reaches a Dulong-Peti limitation value (49.7 $\text{Jmol}^{-1}\text{K}^{-1}$) after 400 K. The calculated heat capacity values are close to each other, and the difference is less than that of bulk modulus and thermal expansion coefficient. At transition pressure, the change is like that of bulk modulus and thermal expansion coefficient. The changed thermodynamic properties can be used to determine the phase transition. Our thermal calculations provide important parameters for the potential applications of ZnO in the future.

The Debye temperature is the cutoff temperature of phonon excitation and freezing. The phonon will go through excitation above the Debye temperature, while the phonon will be freezing below the Debye temperature. The Θ of the B4 phase is 559.3 and 637.2 K at 0 and 30.1 GPa. In the WC phase, the Θ values are 462.2, 560.9, 681.9, and 784.8 K at 30.1, 70, 110, and 157.8 GPa, respectively. The Θ for the B2 phase is 563.6 K at 157.8 GPa. It is observed that the Θ increases with increasing pressure while nearly keeps constant with increasing temperature. The



Fig. 4. (a) Band structure of B4 phase under 0-30.1 GPa by increasing 5 GPa step; (b) band structure of WC phase at (30.1, 70, 110 and 157.8 GPa); (c) band structure of B2 phase at 157.8 GPa; band gap versus pressure graph for B4 phase (d) and WC and B2 phase ZnO (e).

free energy is expressed by the equation F = U-*TS*. In the equation, U represents the internal energy, whereas T and S are temperature and entropy, respectively. We plotted free energy versus temperature graph for the B4, WC, and B2 phases at different pressure in Fig. 3e. The graph demonstrates that the energy decreases with increasing temperature and increases with increasing pressure.

3.3. Band gap and band structure

Band structure and gap are important factors in inducing the novel electronic and optical properties of materials. Bands exploration by the hybrid functional B3LYP method is discussed in this paragraph. Fig. 4a and 4d display the band structure and band gap of the B4 phase in the



Fig. 5. The calculated total DOS and partial DOS of (a) B4 phase ZnO at 0 & 30.1 GPa; (b) WC phase at (30.1, 70, 110 and 157.8 GPa); (c) B2 phase at 157.8 GPa. The horizontal line at 0 is the Fermi level between the valence and conduction band.

pressure range 0–30.1 GPa. The calculated band gap value in this study, i.e., 3.44 eV for B4 phase ZnO (@0 GPa), is as accordingly as reported in previous reports [61]. According to the results, the band gap progressively increases with the increase in pressure. The valence band shifts to the low energy because the hybridization of Zn and O states is enhanced. In contrast, the conduction band value increases to a higher level due to increased repulsion between the electronic states of Zn and O atoms. The repulsion is the result of pressure-decreased bond and an increase in electronic cloud repulsion. The repulsion of the electronic cloud shifts the conduction band to higher energy.

The calculated bands of the WC phase at transition pressures (30.1–157.8 GPa) are given in Fig. 4b, 4e. The wider band gap infers that the WC phase is an insulator, and it has significant applications in shortwave range & at high temperature conditions. To validate the evolution law of the band gap for the WC phase, we have also done the calculations at 50, 70, 90, 110 & 130 GPa. In result the band gap gradually increased from 3.23 eV to 3.68, 4.10, 4.44, 4.75, 5.02 & 5.37 eV respectively. The resulted values of band gap confirm that there is a relation between pressure and band gap: band gap expands by increasing pressure. An increase in the band gap tends to change the electronic properties, and the blue shift of optical properties is also induced due to the increasing band gap. Furthermore, it also results in a shifting of the conduction band to a higher level and the valence band to a lower level. The band shifts are caused due to the same reasons, as explained for the B4 phase previously. In this calculation, the band gap of WC phase ZnO is fitted by a quadratic equation $E_g = 2.50 +$ $0.0261p - 5.11 \times 10^{-5}p^2$. The E_g represents energy (eV), where p is pressure (GPa). This equation also can be applied to detect the WC phase and to measure the pressure at standard calibration. The calculated band gap and band structure of the B2 phase at 157.8 GPa are also shown in Fig. 4c. The B2 phase also possesses a wider band gap, i.e., 4.58 eV.

3.4. Electronic density of states

The electronic density of states is also responsible for persuading the optical properties. The calculated total electronic density of states (DOS) and partial density of states (PDOS) for B4, WC, and B2 phase under transition pressures 30.1 and 157.8 GPa are shown in Fig. 5. To explore and evaluate the gradually changed DOS of WC phase, it is also calculated at 70 and 110 GPa. The Fermi level is fixed as 0 eV. The energy which divides the lower and upper parts of the valence band in the B4 phase (@30.1GPa) is -6.0, WC phase (@30.1, 157.8 GPa) is -6.8, -6.5, and B2 phase (@157.8 GPa) is -7.5 eV. Change in pressure improves the hybridization, expands the DOS, and shifts the peaks of the valence and conduction band to low as well as high energy levels. Expansion is associated with band structures, and it is derived from the repulsion in the ZnO bond. The acquired shifts, expansion, and variation in the shape of peaks lead to the rise in unique optical properties. The relation between total and partial DOS of B4, WC, and B2 phases is similar. The DOS of the WC phase is discussed as an example in this paragraph.

Fig. 5b shows that the value of the valence band produced (-9.90 eV) at transition pressure 30.1 GPa is a combination of upper and lower parts. The upper part (-6.5-0 eV) arises from the O 2*p* state and the lower part (-9.9-6.5 eV) from the Zn 3*d* state. Simultaneously, the valence band (-20.8-17.4 eV) is derived from O 2*s* state, while the conduction band is derived from Zn 4*s* State. Furthermore, in the second part at 157.8 GPa, the valence band energy (-12-0 eV) is divided into two parts. The energy (-6.8-0 eV) accredited to O 2*p* state and the energy (-12.0-6.8 eV) to the Zn 3*d* state. The valence energy range between (-23.5-18.9 eV) comes from the O 2*s* state. The Zn 4*s* state is responsible for producing corresponding conduction bands. The Zn-O bond is induced due to the strong hybridization of Zn 3*d* and O 2*p* states, which express that ZnO is covalent in nature.

3.5. Optical properties

3.5.1. Dielectric function

Dielectric function $(\varepsilon(\omega))$ and optical constants are essential to understand as well as for the description of optical properties. In order to investigate the optical changes caused by the change in pressure, we calculated dielectric function and optical properties under 0–157.8 GPa. The equation of dielectric function is given as $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, in which the $\varepsilon_1(\omega)$ is the real part and $\varepsilon_2(\omega)$ is the imaginary part. It expresses the response of ZnO to photon excitations.

$$\varepsilon_2(\omega) = \frac{2e^2\pi}{\varepsilon_0} \sqrt{\Psi_k^c \hat{u} \cdot r \Psi} \langle \Psi_k^c \hat{u} \cdot r \Psi \rangle_k^\nu (E_k^c - E_k^\nu - E)$$
(8)

In Eq. (8), ω is the frequency of photons incident through a crystal. The superscripts *c* and *v* represent the respective conduction and valence bands. The real part $\varepsilon_1(\omega)$ was calculated by using the Kramers-kronig relation (Eq. (9)) [62]

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega' 2 - \omega^2} d\omega'$$
(9)

The function *P* denotes the integral constant.

Fig. 6a, c, and e present the calculated imaginary part $\varepsilon_2(\omega)$ of B4, WC, and B2 phase ZnO, the photon energy ranges from 0 to 55 eV. The starting values for B4 and WC phase at 30.1GPa are 3.18 & 3.40 eV, whereas the starting values for WC and B2 phases are 5.4 & 7.5 eV at 157.8 GPa. It is noticed that in comparison with the B4 phase, the profile of the WC phase is more expanded between 4.2 and 50 eV. The expansion effect is linked to the expansion in DOS, and it indicates that the WC phase has potential properties in the wider ultraviolet range. At transition pressure 30.1 GPa, the WC phase has three main peaks (9.7, 11.5 & 13.0 eV), which represents the phase transition from B4 to the WC phase. Simultaneously in high energy region, by increasing pressure (30.1-157.8 GPa) the peaks (around 9.7, 11.5, 13.0, 15.6 & 20.1 eV) shift to higher values (around 12.1, 15.9, 18.1, 20.0 & 22.7 eV). The blue shift and a small change in profiles of peaks are associated with the increasing band gap (3.23-5.37 eV). The peaks at around 9.7, 11.5, 13.0 & 15.6 eV mainly originate from the Zn 3d and O 2p states [63,64], whereas, peak at around 20.1 eV attributed to the O 2s and Zn 3d states. The presence of a peak at around 14.0 eV for the B2 phase at 157.8 GPa epitomizes the transition of WC to the B2 phase. In addition, all the acquired peaks of $\varepsilon_2(\omega)$ obeyed the selective rules and are in accordance with the electronic transitions between low and high energy states.

Real part $\varepsilon_1(\omega)$ plays an imperative role in identifying the applications of WC phase ZnO. $\varepsilon_1(0)$ values obtained for B4, WC, and B2 phase (shown in Fig. 6 b, d, and f) are 2.6, 3.1 & 3.3 eV, respectively. These results demonstrate that the pressure has a minute effect on $\varepsilon_1(\omega)$ in the low energy region. $\varepsilon_1(\omega)$ of B4 and WC phase increases slowly, and there is a small change in its shape below 11.0 eV, after that, a rapid drop in peaks is observed. Besides, the B2 phase maintains a constant value below 3.4 eV. The constant values indicate the dielectric nature of B4 and WC phase in the wider region and B2 phase in the visible region. With the increase in pressure, the static $\varepsilon_1(0)$ shifts from 2.6 to 3.1 eV and then to 3.3 eV. These shifts can be used to identify the transitions from B4 to WC and then to the B2 phase correspondingly. In the high energy region beyond 50.0 eV, the $\varepsilon_1(\omega)$ values and profile for three phases become almost the same. This implies that the three phases show different behaviour and properties below 50.0 eV. Interestingly, some peaks of $\varepsilon_1(\omega)$ are found in the deep negative region. The Peak drop to the negative region indicates the change of dielectric behaviour of materials to a metallic behaviour. Dielectric behaviour represents the small number of carriers in material, whereas the materials with metallic behaviour are rich in carriers. According to the resulted values of negative $\varepsilon_1(\omega)$, the B4 phase exhibits metallic behaviour at around 19.0 eV. The WC phase is observed to behave metallic in nature at 21.9 eV



Fig. 6. The calculated imaginary $\varepsilon_2(\omega)$ (a) (c) (e) and real $\varepsilon_1(\omega)$ (b) (d) (f) parts of dielectric functions for B4 phase (0–30.1 GPa), WC phase and B2 phase (0–157.8 GPa).

and 23.5 eV while that of the B2 phase at around 26.0 eV. The determined dielectric and metallic properties are essential for the future application of WC phase ZnO.

3.5.2. Optical constants

Optical constants such as absorption coefficient ($\alpha(\omega)$), reflectivity ($R(\omega)$), the real part of the refractive index ($n(\omega)$), and the loss function ($L(\omega)$) are considered as significant functions in manufacturing the

optoelectronic devices. In the present work, the optical constants were calculated by equations (10)-(13).

$$\alpha(\omega) = \sqrt{2\omega} \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{1/2}$$
(10)

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$$R(\omega) = \left| \frac{\sqrt{\varepsilon_1(\omega) + i\varepsilon_2(\omega)} - 1}{\sqrt{\varepsilon_1(\omega) + i\varepsilon_2(\omega)} + 1} \right|^2$$
(11)

$$n(\omega) = \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} + \varepsilon_1(\omega)\right]^{1/2} / \sqrt{2}$$
(12)

$$L(\omega) = \frac{\epsilon_2(\omega)}{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)}$$
(13)

Optical constants calculated under photon energy range 0–55.0 eV are given in Figs. 7–9. The results demonstrate that the optical constants undergo a blue shift with an increase in pressure. The peak shift increases with increasing pressure for all the optical constants. We have taken $\alpha(\omega)$ as an example to discuss the relation between pressure and



Fig. 7. The calculated absorption $\alpha(\omega)$ of (a) B4 (b) WC (e) B2 phase ZnO; (c) enlarge absorption of WC phase from pressure 0 to 157.8 GPa; (d) position of E_A with respect to pressure.



Fig. 8. The calculated reflectivity $R(\omega)$ and real part of refractive index $n(\omega)$ versus energy under pressure of B4, WC and B2 phase ZnO: (a) (b) (c) $R(\omega)$; (d) (e) (f) $n(\omega)$.

positions of peak E_A , and similar relations can be applied to other optical constants. Fig. 7a and b shows that $\alpha(\omega)$ lies in the ultraviolet region prior to the phase transition from B4 to the WC phase. The $\alpha(\omega)$ of the WC phase has a wider area, which indicates its widespread applications. We have taken the peak "A" to investigate the phase transitions. Fig. 7c shows an enlarged view of absorption peaks for the WC phase under pressure. A clear shift in Peak "A" is observed at 4.7 eV after the B4 \rightarrow WC transition at 30.1 GPa. Peak "A" steadily increases with increasing pressure and undergoes a blue shift (6.7 eV) at pressure 157.8 GPa. The

increased peak of the B2 phase produced at 11.0 eV reflects the transition of the WC phase to the B2 phase. The shift in peaks is proportional to change in DOS and an increase in the band gap. The position of peak E_A has a blue shift with increasing the pressure between the range 30.1 to 157.8 GPa, which is expressed by plotting a graph (Fig. 7d). We used an equation $E_A = 4.16 + 0.0219p - 3.73 \times 10^{-5}p^2$ to fit the relation, E_A and p are calculated in units eV and GPa. The blue shift of absorption peaks is important for measuring the pressure after careful calibration.

The reflected energy ratio of incident light $R(\omega)$ (reflectivity) is also a





Fig. 9. The calculated loss function $L(\omega)$ versus energy under pressure of (a) B4, (b) WC and (c) B2 phase ZnO.

major optical constant. The results given in Fig. 8 a, b, and c asserts that, $R(\omega)$ values of B4 and WC phase remains almost constant below 3.4 eV whereas B2 phase keeps constant value below 3.7 eV. The two increased peaks at 9.6 eV and 11.0 eV are produced due to corresponding phase transitions from B4 \rightarrow WC \rightarrow B2. The maximum peak value of $R(\omega)$ for B4 phase (@30.1 GPa) is about 19.0 eV. Simultaneously, the maximum $R(\omega)$ for WC phase (@30.1, 157.8 GPa) is 21.9 and 23.5 eV, for B2 phase (@157.8 GPa) is around 26.0 eV. These values are matched fine with the negative $\varepsilon_1(\omega)$ results. In addition, the maximum reflectivity ratio in this calculation is found to be 27% for B4 phase, 22% for WC phase and 43% for B2 phase. The results declare that B2 phase have higher ratio of incident light. The $R(\omega)$ go through peaks drop at 21.5, 23.9 eV for B4, 24.5, 29.3, 31.2 eV for WC and 27.0, 37.5, 38.5 eV for B2 phase. The peak drop positions are in correspondence with the maximum peak points of $L(\omega)$.

According to the profile shown in Fig. 8 d, e and f, the shape of the real part of refractive index $n(\omega)$ is similar to $\varepsilon_1(\omega)$. The $n(\omega)$ of B4 phase at 30.1 GPa starts at 1.6 eV and it increases smoothly below 13.0 eV, after that a continues peak drop is observed. The peak drop should be noted for the applications. B4 and WC phase possesses almost same type of profile at same applied pressure, except the starting value shifted to 1.77 eV. Additionally, an increased peak (10.9 eV) is produced, which represents the phase transition from B4 to WC phase. By increasing the pressure to 157.8 GPa, the starting value of B2 phase increased to 1.84 eV. Furthermore, two new peaks of almost the same height around 2.5 produced at 9.5 eV & 13.5 eV displays the transition of WC to B2 phase. The immediate peak drop of B2 phase also should be noted for applications.

The loss function $L(\omega)$ defines the loss in energy of the light transmitted through the crystal. Under given pressure, peaks of $L(\omega)$ expresses plasma resonance in the used crystal (ZnO) and their emergence is followed by the decline in the peaks of $R(\omega)$. As given in Fig. 9, the two major extreme peaks of B4 phase at 21.5 & 23.9 eV possess almost the same value as those of declining peaks of $R(\omega)$. In the low energy range (3.0–15.0 eV) the $L(\omega)$ increases slowly and gradually, after that a sudden increase is observed. The WC phase ZnO has mainly three increased peaks (24.5, 29.3 & 31.2 eV) which indicate the B4 to WC phase transition. Three high and enhanced peaks (27.0, 37.5 & 38.5 eV) of B2 phase clearly recognize the phase transition from WC to B2. The *L*(ω) becomes approximately zero beyond 58.0 eV. The value of $L(\omega)$, starting energy values of $\alpha(\omega)$ and $n(\omega)$ are 0, 0 and 1.7 under visible region (1.61–3.10 eV). These results reveal that the WC phase ZnO possesses a transparent nature.

4. Conclusions

In this study the structural, thermodynamic, electronic and optical properties of WC (B_h) phase ZnO have been explored. The calculated enthalpies evidenced that the transformation of wurtzite B4 phase to WC phase followed by the WC phase transform to B2 phase ZnO at 30.1 & 157.8 GPa respectively. The acquired transition pressure and lattice constants were found to be accordingly as reported. The bulk modulus decreases with increasing temperature while the coefficient of thermal expansion and heat capacity increases with increasing temperature. The thermodynamic property values increase at transition points which can be used to determine the phase transition. The comprehensive analysis

of electronic and optical properties of WC phase with B4 and B2 phase showed that the band gap of WC phase is directly proportional to the pressure i.e., band gap increases by increasing the pressure. Investigations declared that, the increase in pressure leads to the shifting of valence as well as conduction band at a low & high energy level respectively. The relations between band-DOS, $\varepsilon_2(\omega)$ -DOS and $R(\omega)$ - $L(\omega)$ are discussed. The band gap, real part of dielectric function $\varepsilon_1(\omega)$ and optical constants calculation confirmed the insulator, metallic and transparent nature of the WC phase under different conditions. Thus, it is concluded that presented research is a robust source of techniques for the identification of the WC phase, which can be successfully applied for the designing of a variety of new devices.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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