

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/258653376>

# a Comprehensive DFT Study of Zinc Oxide in Different Phases

Article in International Journal of Modern Physics C · June 2012

DOI: 10.1142/S012918311250043X


CITATIONS

8

READS

672


4 authors:



**Bakhtiar Ul Haq**  
King Khalid University

74 PUBLICATIONS 336 CITATIONS


SEE PROFILE



**Afaq A**  
University of the Punjab

61 PUBLICATIONS 408 CITATIONS


SEE PROFILE



**Rashid Ahmed**  
Universiti Teknologi Malaysia

130 PUBLICATIONS 1,100 CITATIONS

SEE PROFILE



**Shahzad Naseem**  
University of the Punjab

629 PUBLICATIONS 2,639 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:

Project

Density functional studies on 100 Novel Perovskites. [View project](#)

Project

Thin Film Solar Cells [View project](#)

## A COMPREHENSIVE DFT STUDY OF ZINC OXIDE IN DIFFERENT PHASES

BAKH TIAR UL HAQ<sup>\*,†</sup>, A. AFAQ<sup>\*</sup>, R. AHMED<sup>†,‡</sup> and S. NASEEM<sup>\*</sup>

*<sup>\*</sup>Center of Excellence in Solid State Physics  
University of the Punjab, Quid-e-Azam Campus  
Lahore 54590, Pakistan*

*<sup>†</sup>Department of Physics, Faculty of Science  
Universiti Teknologi Malaysia  
81310 Johor Bahru, Johor, Malaysia  
<sup>‡</sup>rashidahmed@utm.my*

Received 24 March 2012  
Accepted 26 April 2012  
Published 15 June 2012

A density functional study for structural and electronic properties of Zinc Oxide (ZnO), in wurtzite, rock salt and zinc-blende phases has been performed using full potential-linearized augmented plane wave/linearized augmented plane wave plus local ideal orbital (FP-LAPW/L (APW+lo) approach as realized in WIEN2k code. To approximate exchange correlation energy and corresponding potential, a special GGA parameterized by Wu–Cohen has been implemented. Our results of lattice constants, bulk moduli as well as for internal parameter with GGA-WC are found to be more reliable. This study reveals that value of internal parameter decreases with increasing volume whereas computed electronic band structure confirms the direct band gap behavior of ZnO in B4 and B3 phases while indirect band gap behavior in B1 phase. Moreover, two fold degeneracy at the maxima of valence band for B4 and B1 phases whereas three fold for B3 is observed. A detailed comparison with experimental and other first principles studies is also made.

*Keywords:* ZnO; density functional theory; generalized gradient approximation; semiconductors; electronic structure.

PACS Nos.: 71.15.Mb, 71.20.Nr, 71.20.±b.

### 1. Introduction

ZnO is one of the most important II–VI binary compound, being a wide and direct band gap semiconductor, has many potential applications in electronics and optoelectronic devices. Extensive research work is going on this material from a long time because of its application as a base material in light emitting devices and its expected potential applications in near future in laser diodes, UV filters, transparent

<sup>\*</sup>Corresponding author.

field effect transistors, blue/UV optoelectronics and transparent electronic circuits, etc.<sup>1–4</sup> The applications of ZnO may further be enhanced and novel features may be exposed with the further study of its physical properties.

Physically ZnO exists in three different structural phases, room temperature stable wurtzite (B4), high pressure rock salt (B1) and zinc-blende (B3). Due to its commercial value, considerable number of experimental as well as theoretical studies related to different phases and properties are found in literature.<sup>1–23</sup> Karzel *et al.*<sup>5</sup> investigated phase transition experimentally as well as theoretically using full potential linearized augmented plane wave (FP-LAPW) method. Jaffe and Hess<sup>6</sup> employed Hartree–Fock (HF) approach to calculate the ground state total energy. Jaffe *et al.*<sup>7</sup> also analyzed the band structure and total energy of ZnO using local density approximation (LDA) and generalized gradient approximations (GGA) within density functional theory (DFT). Yu *et al.*<sup>9</sup> explored structural and electronic properties of ZnO in B4 phase at simple GGA level in DFT. Amrani *et al.*<sup>10</sup> performed study under high pressure to investigate phase transition using FP-LAPW method with LDA. Later on same study was followed by Schouxin *et al.*<sup>11</sup> using the ultra-soft pseudo-potential approach.

Quality of DFT investigations is crucial to the proper choice of exchange correlation functional for energy and corresponding potential. Although an extensive amount of theoretical and experimental investigations are available on ZnO, to the best of our knowledge a comprehensive study with Wu–Cohen parametrized GGA is rarely found for this important material which is considered to be simple and more accurate for solids<sup>24</sup> as compared to other forms of available GGA.

In this research work, we investigate the effect of new GGA parametrized by Wu–Cohen (GGA-WC) on the structural and electronic properties of B4, B1 and B3 phases of ZnO using FP-(L(APW+lo)) method as implemented in WIEN2k code and give a comparison of results obtained with GGA-WC to experimental and previously calculated results using other forms of GGA. Our paper is organized as: in Sec. 2, we describe computational details of our calculations, in Sec. 3, results and discussion has been reported. At the end in Sec. 4, conclusions are drawn.

## 2. Computational Details

In this study we used full potential-linearized augmented plane wave plus local orbital FP-(L(APW+lo)) method designed within DFT<sup>25</sup> to calculate structural and electronic properties of ZnO. Although FP-(L(APW+lo)) as implemented in WIEN2k software package, is one of the most precise DFT-based approach for the calculations of electronic structure of solids, predicts results comparable to experiment for many physical properties, it badly underestimate the bandgap energy in case of semiconductors and insulators. It is because DFT is principally for ground state properties and to cope with excited state properties and produce results in consistent with experimental measurements, it requires an exact form of exchange correlation energy functional and corresponding potential. Unluckily no exact form

of this functional exists in nature except uniform electron gas. However, to overcome this drawback of DFT, different approximated forms of the exchange correlation energy functional and corresponding potential have been introduced in literature. In this work, computations were performed using GGA-WC<sup>24</sup> as available in WIENE2k software package<sup>26,27</sup> which is considered as one of more accurate functional for solids. To carry out these calculations, unit cell in this scheme, is partitioned into atomic spheres [called muffin tin(MT)] and interstitial region. Inside MT sphere a spherically symmetric potential is assumed, while outside it is taken to be constant. In this scheme core electrons are treated fully relativistically and valence are treated semi-relativistic. Inside the MT sphere, the wave function is expanded as a linear combination of radial function times the spherical harmonics with  $\ell = 9$  whereas a plane wave expansion is used in interstitial region. We treated 3d and 4s electrons of Zn, and 2s and 2p electrons of O as the valence electrons. In our calculations  $R_{\text{MT}}$  values have been used 1.77 a.u. and 1.57 a.u. for Zn and O, respectively and a mesh of 72 special  $k$  points in the irreducible Brillouin zone, whereas  $R_{\text{MT}} \times K_{\text{max}} = 8.00$  and  $G_{\text{max}} = 16$  is taken to obtain accurate and well converged results.

### 3. Results and Discussion

#### 3.1. Unit cell structure

ZnO at room temperature and atmospheric pressure exhibits thermodynamically stable B4 structure having hexagonal primitive unit cell with space group  $C_{6v}^4 - P6_3mc$ . Each primitive unit cell of ZnO consists of four atoms where two Zn atoms are at the positions  $(1/3, 2/3, 0)$ ,  $(1/3, 2/3, 1/2)$  and O atoms at positions  $(1/3, 2/3, \mu)$ ,  $(1/3, 2/3, \mu + 1/2)$ .  $\mu$  is the internal parameter of the B4 phase that determines the bond-length (anion–cation bond–length) parallel to  $c$ -axis divided by the  $c$ -lattice parameter.<sup>1</sup> The B4 phase unit cell consists of four atoms, where one atom of group-VI is surrounded by four atoms of group-II and vice versa. B1 phase of ZnO that may be found at comparatively high pressure has space group  $Fm\bar{3}m$  (No. 225) and atomic positions are Zn(0, 0, 0) and O(1/2, 1/2, 1/2), while the B3 phase has the atomic positions Zn(0, 0, 0) and O(1/4, 1/4, 1/4) and space group  $Fm\bar{4}3m$  (No. 216).

To determine structural parameters, equilibrium volume of the unit cell in all three phases was obtained from Muranaghan equation of states (EOS).<sup>28</sup> From Table 1 it can be seen that our calculated results of the total energy in all three phases is in close agreement except a slight difference found in B4 phase. Calculated values of lattice constant  $a$ , for B1 and B3 phase, are 4.26 Å and 4.55 Å, respectively whereas for B4 phase, calculated values of lattice constants are  $a = 3.24$  Å,  $c = 5.20$  Å,  $c/a = 1.602$  and  $\mu = 0.3794$ . Our results with GGA-WC are in good agreement to experiment,<sup>5,17–19</sup> whereas results of lattice parameters with other GGA, show overestimation to the experiment.  $c/a$  ratio is also calculated by plotting energy against percentage variation of volume in the range  $-10$  to  $10$  as given in Fig. 1.

Table 1. The calculated lattice parameters of ZnO in three phases B4 (wurtzite), B1 (rocksalt) and B3 (zinc-blende) in comparison with both experimental and theoretical values available in literature are shown.

	Present work	Other theoretical values	Experimental values
Wurtzite (B4)			
$a$ (Å)	3.24	3.27, <sup>9</sup> 3.2077, <sup>10</sup> 3.290, <sup>6</sup> 3.199, <sup>6</sup> 3.1841 <sup>11</sup>	3.24, <sup>18</sup> 3.2496 <sup>5</sup>
$c$ (Å)	5.20	5.24, <sup>16</sup> 5.1636 <sup>10</sup>	5.20 <sup>18</sup>
$c/a$	1.602136	1.619, <sup>11</sup> 1.60976, <sup>10</sup> 1.604, <sup>5</sup> 1.593, <sup>6</sup> 1.615 <sup>16</sup>	1.6021, <sup>17</sup> 1.6018 <sup>5</sup>
B (GPa)	143.004	132.02, <sup>9</sup> 145.9, <sup>11</sup> 168.4 <sup>10</sup>	143, <sup>18</sup> 183 <sup>5</sup>
dB/dP	4.5844	4.82, <sup>9</sup> 4.34, <sup>10</sup> 4.4, <sup>5</sup> 3.6, <sup>6</sup> 4.5 <sup>16</sup>	4.68, <sup>18</sup> 4, <sup>5</sup> 3.6 <sup>17</sup>
$\mu$	0.3794	0.38031, <sup>11</sup> 0.3795, <sup>10</sup> 0.381, <sup>5</sup> 0.3856, <sup>6</sup> 0.379, <sup>16</sup>	0.3819 <sup>5</sup>
$E_0$ (eV)	-3741.6870		
Rock salt (B1)			
$a$ (Å)	4.267	4.211, <sup>10</sup> 4.22 <sup>11</sup>	4.28 <sup>17</sup>
B (GPa)	196.5921	210.1, <sup>10</sup> 209.6 <sup>11</sup>	202.5 <sup>17</sup>
dB/dP	5.00	4.44, <sup>10</sup> 4.46 <sup>11</sup>	3.54 <sup>17</sup>
$E_0$	-3741.6713		
Zinc blende (B3)			
$a$ (Å)	4.55	4.49, <sup>10</sup> 4.52 <sup>11</sup>	4.58 <sup>19</sup>
B (GPa)	146.2713	168, <sup>10</sup> 169.5 <sup>11</sup>	
dB/dP	4.6260	4.66, <sup>10</sup> 4.33 <sup>11</sup>	
$E_0$	-3741.6861		

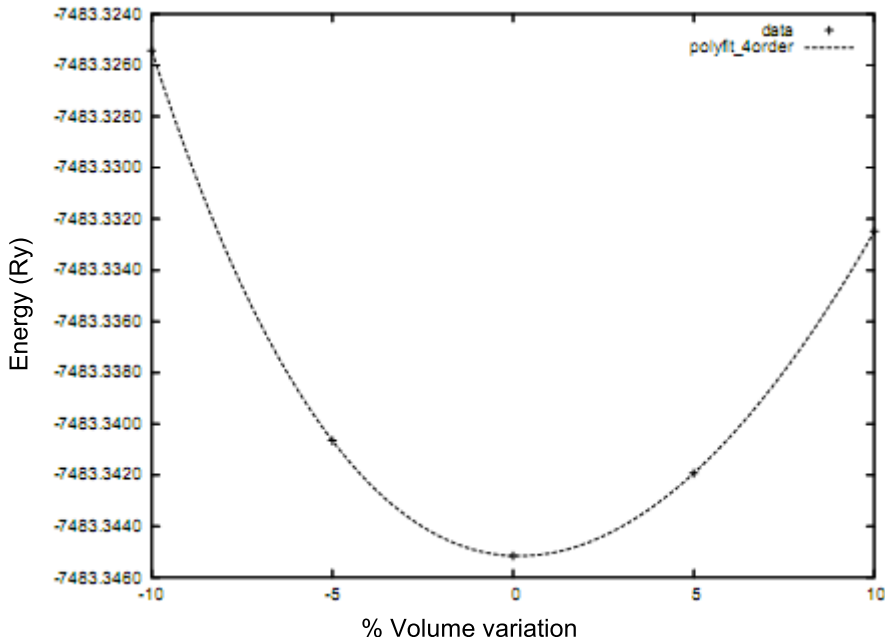


Fig. 1. Total energy vs unit-cell percentage volume variation. Data is fitted in fourth-order polynomial. The unit cell total energy minimum occurs at equilibrium volume.

### 3.2. Variation of volume with pressure

We also investigated the volume as well as lattice parameters of the unit cell of ZnO for discrete values of external pressure over a range from  $-15$  to  $35$  GPa. From Fig. 2 it seems inversely proportional variation of volume with pressure. This  $P$ – $V$  curve was obtained by putting the data in Eq. (1).

$$P(V) = \frac{3B}{2} [(V_0/V)^{7/3} - (V_0/V)^{5/3}] * \left[ 1 + \frac{3}{4}(B' - 4)[((V_0/V)^{2/3} - 1)] \right]. \quad (1)$$

The effect of pressure on both lattice constants “ $a$ ” and “ $c$ ” in B4 phase is shown in Fig. 3. Our data plots for both lattice constants ( $a$  and  $c$ ) show continuous decrease in size with increasing pressure in all ranges.

Figure 4 shows the effect of percentage variation of volume on  $\mu$ -parameter. This  $\mu$ - $V$  plot is obtained by substituting values of lattice constants  $a$  and  $c$  in Eq. (2). These  $a$  and  $c$  values were obtained by the variation of volume in the range  $-10\%$  to  $10\%$  in relation.<sup>1</sup>

$$\mu = \left( \frac{1}{3} \right) \left( \frac{a^2}{c^2} \right) + \frac{1}{4}. \quad (2)$$

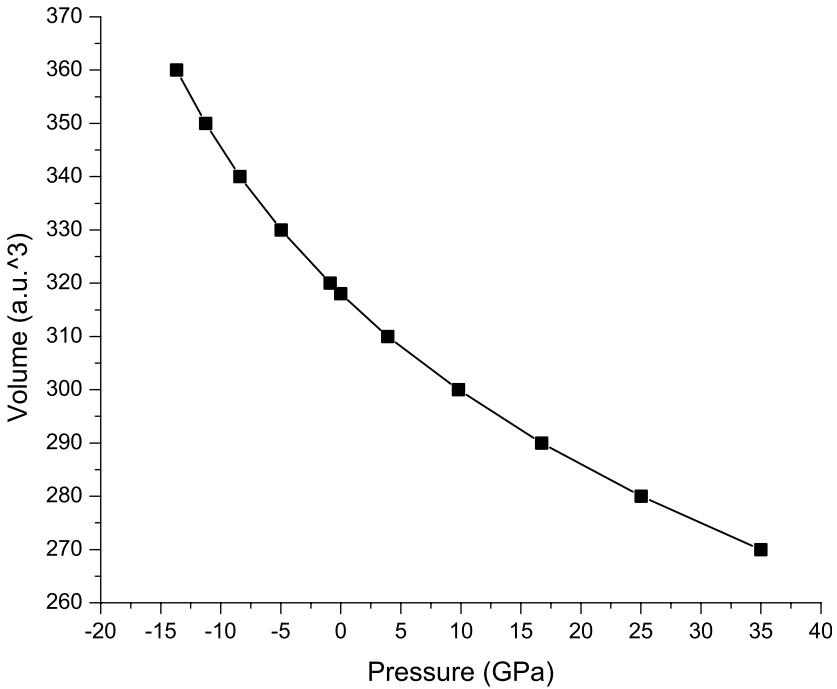


Fig. 2. Variation of volume  $V$  of the unit cell of wurtzite ZnO with pressure  $P$ . Data points are fitted in Murnaghan EOS ( $P$ – $V$ ).

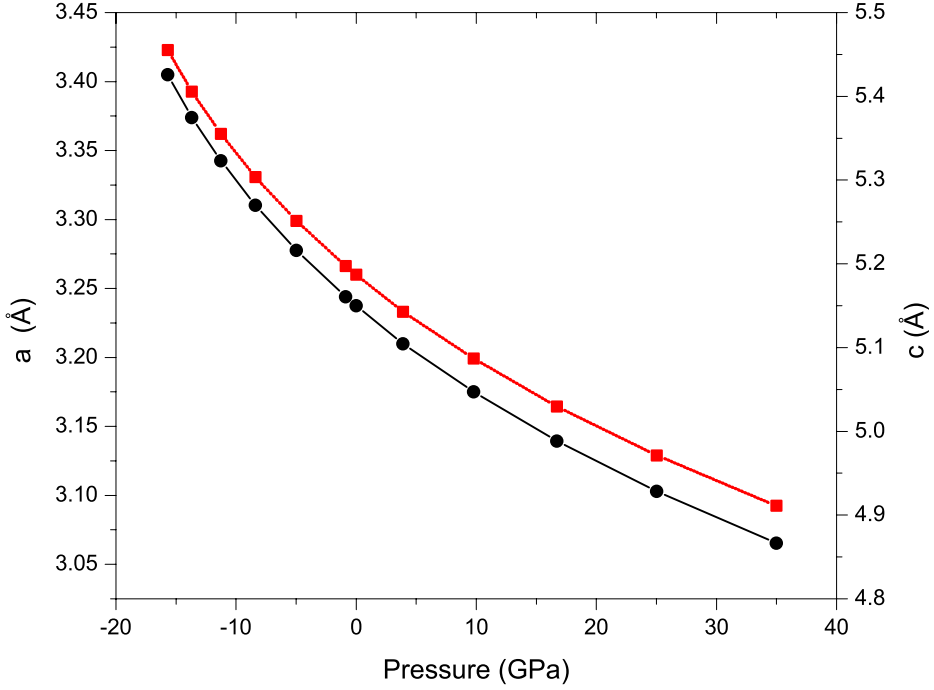


Fig. 3. (Color online) The pressure-dependent behavior of the lattice constants “ $a$ ” and “ $c$ ” in wurtzite phase has been shown. The solid line represents the variation of  $a$  and the dashed line represent variation of  $c$  with pressure.

The  $\mu$ -V plot indicates that internal parameter decreases with increasing value of unit cell volume (Fig. 4).

### 3.3. Band structure and density of states

The band structure of ZnO in three phases are evaluated using calculated lattice parameters (for B4,  $a = 3.24$  Å,  $c = 5.20$  Å and  $\mu = 0.3794$ , for B1,  $a = 4.267$  Å and for B3,  $a = 4.55$  Å). Evaluated band gap values are listed in Table 2 and corresponding band structure for B4, B1 and B3 phases are shown in Fig. 5. Energies of conduction band and valence band are arranged in such a way that fermi level lies at zero energy.

From Fig. 5 it can be seen that the valence band maxima and conduction band minima lie on the same  $\Gamma$  point for B4 and B3 phases, indicating direct band behavior of B4 and B3 phase. For B1 phase the valence band minimum lies at “L” point and conduction band minimum lies on  $\Gamma$  point which reveals the indirect band gap nature of this phase. Figure 5 also shows that valence band of ZnO exhibit two-fold degenerate energy levels at fermi level for B4 and B1 phase where a three-fold degenerate energy level exists in case of B3. From Table 2 it is evident that our computed values of band gap are in fair agreement with other theoretical calculations, our

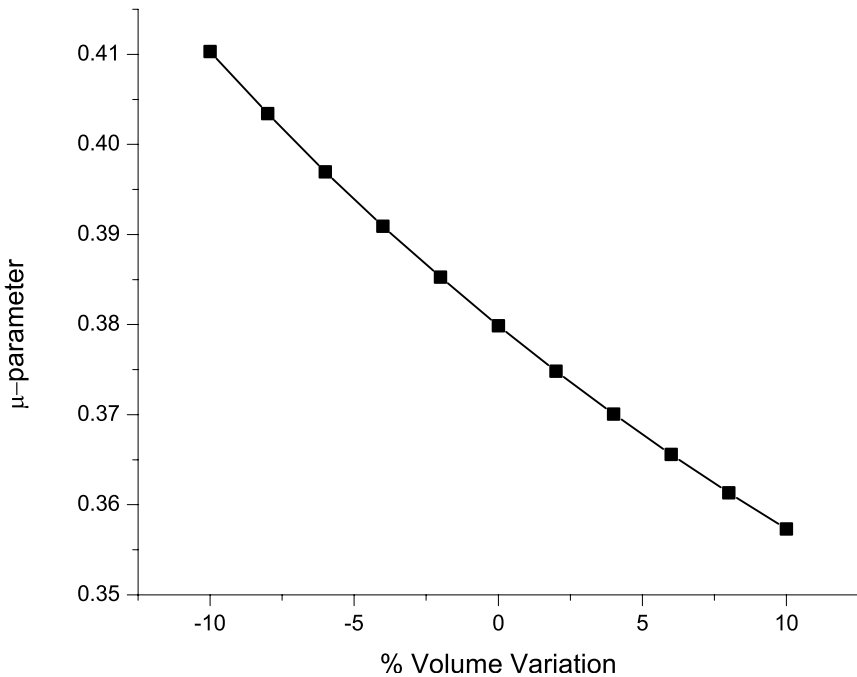


Fig. 4.  $\mu$ -parameter vs the percentage volume variation curve. The  $\mu$ -parameter is a dimensionless quantity and at equilibrium volume of the unit-cell  $\mu = 0.3794$ .

Table 2. A comparison of calculated band gap energies with experimental and other theoretically calculated data has been shown for ZnO in three structural phases B4 (wurtzite), B1 (rocksalt) and B3 (zinc-blende).

	Present work	Experimental values	Other calculations
ZnO (B4)			
$\Gamma$ - $\Gamma$	1.2	3.3 <sup>1</sup>	11.70, <sup>6</sup> 0.81, <sup>10</sup> 0.77, <sup>15</sup> 0.78, <sup>15</sup> 2.44, <sup>15</sup> 11.39, <sup>15</sup> 0.80, <sup>11</sup>
$M$ - $M$	6.3		6.73, <sup>10</sup> 6.79 <sup>11</sup>
$K$ - $K$	8.4		9.40, <sup>10</sup> 9.30 <sup>11</sup>
$A$ - $A$	3.2		3.90, <sup>10</sup> 3.91 <sup>11</sup>
ZnO (B1)			
$\Gamma$ - $\Gamma$	3.8		2.6, <sup>10</sup> 3.09 <sup>11</sup>
$L$ - $L$	6.2		5.42, 5.43 <sup>11</sup>
$K$ - $K$	8		6.67, <sup>10</sup> 8 <sup>11</sup>
$X$ - $X$	7.5		
$W$ - $W$	8.6		9.23, <sup>10</sup> 9.57 <sup>11</sup>
$L$ - $\Gamma$	1.5	2.45 <sup>20</sup>	1.10, <sup>10</sup> 0.75 <sup>12</sup>
ZnO (B3)			
$\Gamma$ - $\Gamma$	0.70		0.65, <sup>12</sup> 3.75, <sup>21</sup> 0.64, <sup>22</sup> 3.59 <sup>23</sup>
$K$ - $K$	7.9		
$X$ - $X$	7.3		
$L$ - $L$	6.2		
$W$ - $W$	9.3		



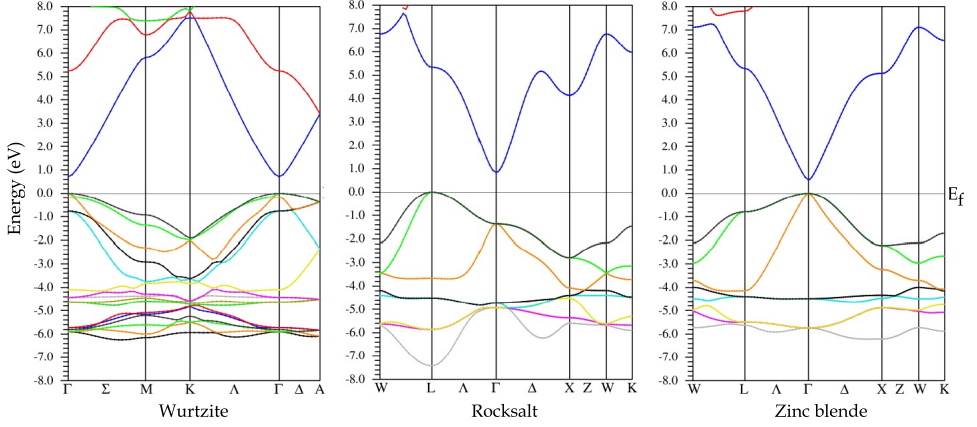


Fig. 5. (Color online) Band structure of ZnO for wurtzite, rocksalt and zinc-blende phases at  $P = 0$  GPa.

calculated band gap values with GGA-WC are smaller than experimental results indicating that this form of GGA is also not sufficiently flexible to give consistent results for band gap energy similar to other forms of GGAs and LDA. Our calculated band gap value for B4 phase is about 63.6% and for B1 about 39.8% less than that of experimentally<sup>1,20</sup> reported band gap values.

The densities of states in B4, B1 and B3 phases are shown in Fig. 6, it is observed that mainly valence bands are originated from Zn-3d states together with O-2p states

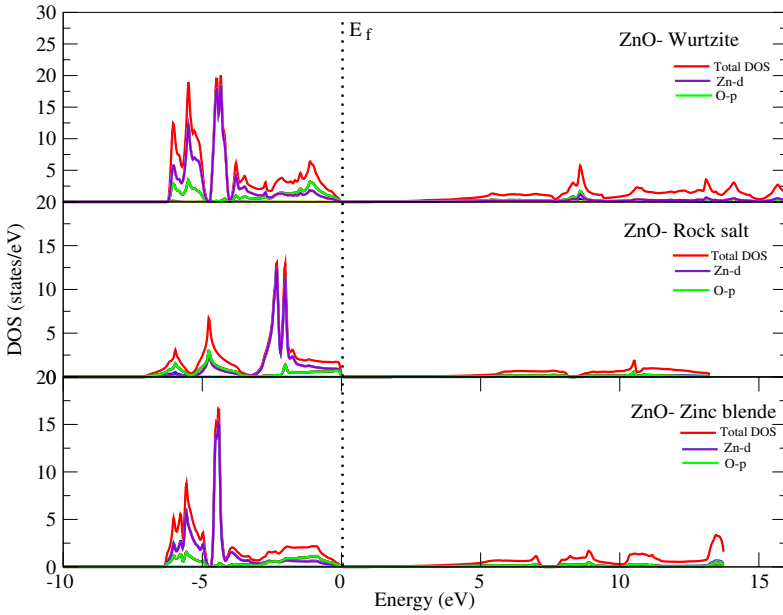


Fig. 6. (Color online) Total density of states of ZnO for wurtzite, rocksalt and zinc-blende phases.

whereas the top of valence band is dominated from O-2p states. A significant dispersion of *d* band can be seen in Fig. 6. This high dispersion of *d* band is because of strong hybridization of p and d orbital in the valence band that pushes O-2p states closer to conduction band, resulting in band gap narrowing.

#### 4. Conclusion

In this work, equilibrium lattice constants, bulk moduli, band structure and density of states of ZnO in its stable wurtzite, high pressure rocksalt and zinc-blende phases have been investigated using GGA-WC as an exchange correlation energy functional within a first principles computational approach based on DFT. Our results for structural parameters with GGA-WC are closer to experiment as compared with other forms of GGA. Also numerical values for band gap with GGA-WC are in good agreement with previous GGAs and LDA calculations, however are underestimated to the experiment measurements. Our investigations indicates that GGA-WC gives good results for lattice parameters but show similar behavior regarding bandgap values similar to other GGAs. Analysis of our computed band structure reveals that ZnO in wurtzite and zinc-blende phases is a direct band gap but in rocksalt phase it is indirect band gap semiconductor.

#### Acknowledgment

Authors (Bakhtiar Ul Haq, R. Ahmed) would like to thank for financial support of Ministry of Higher Education (MOHE) Malaysia/Universiti Teknologi Malaysia (UTM) through Grant No. Q.J13000.7126.00J33, FAVF VOTE No. 4D034 and FRGS/1/2012/ST05/UTM/02/2.

#### References

1. U. Ozgur, Y. I. Aliev, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho and H. Morkoc, *J. Appl. Phys.* **98**, 041301 (2005).
2. C. Klingshirn, *Chem. Phys. Chem.* **8**, 782 (2007).
3. C. Klingshirn, M. Grundmann, A. Hoffmann, B. Meyer and A. Waag, *Phys. J.* **5**, 33 (2006).
4. K. Nomura, H. Ohta, K. Ueda, T. Kamiya, M. Hirano and H. Hosono, *Science* **300**, 1269 (2003).
5. H. Karzel, W. Potzel, M. Kofferlein, W. Schiessl, M. Steiner, U. Hiller, G. M. Kalvius, D. M. Mitchell, T. P. Das, P. Blaha, K. Schwarz and M. P. Pasternak, *Phys. Rev. B* **53**, 11425 (1996).
6. J. E. Jaffe and A. C. Hess, *Phys. Rev. B* **48**, 7903 (1993).
7. J. E. Jaffe, J. A. Snyder, Z. Lin and A. C. Hess, *Phys. Rev. B* **62**, 1660 (2000).
8. J. A. Majewski and P. Vogl, *Phys. Rev. B* **35**, 9666 (1987).
9. Z. G. Yu, H. Gong and P. Wu, *J. Cryst. Growth* **287**, 199 (2006).
10. B. Amrani, I. Chiboub, S. Hiadsi, T. Benmessabih and N. Hamdadou, *Solid State Commun.* **137**, 395 (2006).
11. S. Cui, W. Feng, H. Hu, Z. Feng and Y. Wang, *J. Alloys Compd.* **476**, 306 (2009).

12. Z. Charifi, H. Baaziz and A. H. Reshak, *Phys. Stat. Sol. (b)* **244**, 3154 (2007).
13. Y. Saeed, A. Shaukat, N. Ikram and M. Tanveer, *J. Phys. Chem. Solids* **69**, 1676 (2008).
14. S. Saib and N. Bouarissa, *Phys. Stat. Sol. (b)* **244**, 1063 (2007).
15. M. Usuda and N. Hamada, *Phys. Rev. B* **66**, 125101 (2002).
16. J. Serrano, A. H. Romero, F. J. Manjon, R. Lauck, M. Cardona and A. Rubio, *Phys. Rev. B* **69**, 094306 (2004).
17. S. Desgreniers, *Phys. Rev. B* **58**, 14102 (1998).
18. C. F. Cline and D. R. Stephens, *J. Appl. Phys.* **36**, 2869 (1965).
19. S. M. Zhou, H. C. Gong, B. Zhang, Z. L. Du, X. T. Zhang and S. X. Wu, *Nanotechnol.* **19**, 175303 (2008).
20. A. Segura, J. A. Sans, F. J. Manjon, A. Munoz and M. J. Herrera-Cabrera, *Appl. Phys. Lett.* **83**, 278 (2003).
21. A. Qteish, *J. Phys. Condens. Matter* **12**, 5639 (2000).
22. A. Schleife, F. Fuchs, J. Furthmüller and F. Bechstedt, *Phys. Rev. B* **73**, 245212 (2006).
23. M. Oshikiri and F. Aryasetiawan, *Phys. Rev. B* **60**, 10754 (1999).
24. Z. Wu and R. E. Cohen, *Phys. Rev. B* **73**, 235116 (2006).
25. P. Hohenberg and W. Kohn, *Phys. Rev. B* **136**, 864 (1964).
26. K. Schwarz and P. Blaha, *Comput. Mater. Sci.* **28**, 259 (2003).
27. P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvanicka and J. Luitz, *WIEN2K: An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties* (Vienna University of Technology, 2001).
28. F. D. Murnaghan, *Proc. Natl. Acad. Sci. USA* **30**, 244 (1944).