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Pressure effects on the structural, elastic , electronic and optical properties of ZnO from first-principles calculations

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Abstract

First-principles calculations of the structural, electronic, optical and elastic properties of ZnO as a function of the pressure have been performed within density functional theory using Ultra soft pseudo potentials and generalized gradient approximation (GGA) for the exchange and correlation energy. Through our results, we note that the lattice constants decrease with the pressure increasing. Also, the elastic constants C_{11}, C_{12}, C_{13} and C_{33} and the bulk modulus *B* increase with the pressure increasing. However, the elastic constants C_{44}, the Shear modulus (*G*) and Young's modulus (*E*) decrease slowly with increasing pressure, the band gap increases with the pressure increasing and ZnO has direct band. As pressure increases, the static dielectric constants $\varepsilon_1(0)$ and static refraction index *n(0)* decrease. Our calculated results are in good agreement with experimental data and other theoretical calculations.

Keywords: DFT calculation, electronic, optical, elastic, under pressure

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1.Introduction

ZnO is a wide band gap semiconductor and the crystal structure at ambient pressure is the four-fold-coordinated wurtzite structure (B4). It is a II–VI compound semiconductor whose ionicity resides at the borderline between covalent and ionic semiconductor. ZnO is an important material in various field of applications for examples ceramics, piezoelectric, transducers, chemical sensors, varistors, thyristors, catalysis, optical coating, and photovoltaic [1]. The high-pressure behavior of ZnO has also attracted theoretical interest [2,3,4,5]. The first indication of a transition from the low pressure wurtzite phase of ZnO to a high pressure NaCl phase at 10 GPa was reported by Bates et al. [6] and later confirmed by Jamieson [7], and by Yu et al. [8] at 8.3 GPa. Recent EDX studies by Decremps et al. [9,10] indicate that the transition occurs at 9.8 GPa at room temperature.

Our main goal in this work is to present a detailed study of behavior of structural and mechanical properties of ZnO in the wurtzite phase under hydrostatic pressure by using first-principle calculations based on density functional theory (DFT) within generalized gradient approximation (GGA). The plan of the present paper is as follows. Section 2 gives a description of the method as well as some details of the calculations. The calculated structural, electronic, optical and elastic properties of ZnO are presented and discussed in Section 3. Finally, the summary of our main results and conclusion are given in Sec. 4.

2. Computational methods

All calculations are performed based on the plane-wave pseudo-potential density function theory, as implemented in CASTEP package [11]. Vanderbilt ultrasoft pseudo-potentials [12] are employed to describe the electron-ion interactions. The exchange correlation energy is described in the generalized gradient approximation (GGA) using the Perdew-Burke- Ernzerhof (PBE) functional [13]. The structure is optimized with the Broyden-Fletcher-Goldfarb-Shanno (BFGS) [14] method. Pseudo-atomic calculations are performed for Zn: $3d^{10}$ $4s^2$ and O: $2s^2$ $2p^4$. In the structure calculation, the electronic wave functions are expanded in plane-wave basis set with cutoff energy of 700 eV, and the special points sampling integration over the Brillouin zone (9×9×9 k-points) was employed by the Monkhorst-Pack method [15]. The self-consistent convergence of the total energy is 5.0 10^{-7} eV/atom and the maximum force on the atom is 0.01eV/Å.

3. Results and discussions

3.1. Structural properties

The variation in lattice constants with the pressure between 0.0 and 5.0 GPa using GGA approache is depicted in Fig. 1. It can be seen from Fig. 1 that the lattice constants decrease with increase the pressure.

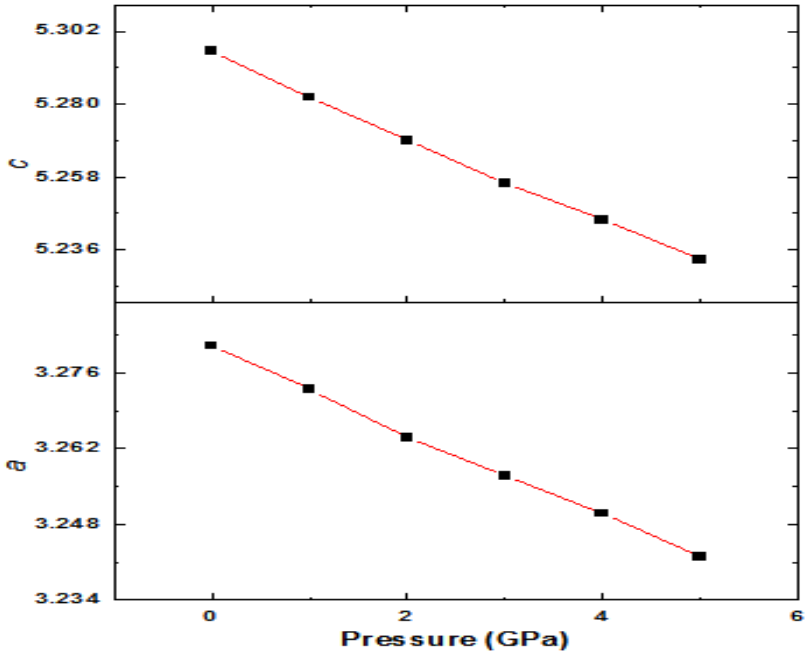

Fig.1. Lattice constants as a function of pressure of ZnO.

The obtained lattice constants (*a*, *c*) for ZnO at T = 0 K and P = 0 GPa are presented in Table 1. Obviously, the calculated lattice constants are well consistent with the experimental values [16-17] and other theoretical results [18-19].

Table 1. Comparison of the ab initio lattice parameters with the corresponding experimental data and theoretical values .

	Present work	Experimental	Other work
a (Å)	3.281	3.258[a] , 3.250[b]	3.292[c] , 3.283[d]
c (Å)	5.296	5.220[a] , 5.204[b]	5.292[c] , 5.309[d]
c/a	1.614	1.602[a] , 1.601[b]	1.607[c] , 1.617[d]

[a] Ref.[16], [b] Ref.[17], [c] Ref.[18] , [d] Ref.[19]

3.2 .Electronic properties

To understand the phase stability from the microscopic point of view, we have also investigated its electronic structures of B4 phase ZnO. Fig. 2 presents band gap at high pressure. It is clear from our results that ZnO at 0 GPa is a semiconductor with a direct band gap of 0.75 eV. The valence band maximum is found to be at the Γ point, and the conduction band minimum is located at Γ point . This result is in good agreement with previous calculation value 0.78eV [20], but much smaller than the experimental value 3.44 eV [21]. It is obvious that the CBM always moves to higher energy, whereas the VBM moves to lower energy, so the band gap broadens.

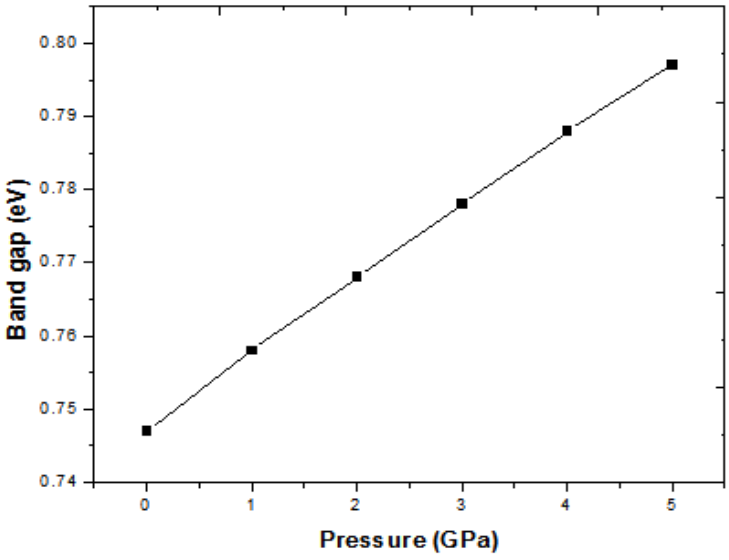

Fig.2. Band gap as a function of pressure.

3.3. Optical properties

In this section, we have calculated frequency dependent optical properties such like complex static of dielectric constant $\varepsilon_1(0)$ and refraction index n(0) at a pressure between 0.0 and 5.0 GPa using GGA approach. Fig. 3 shows the variation of the static dielectric constants and static refraction index as a function of pressure for ZnO .It is obvious that, as pressure increases, the static dielectric constant $\varepsilon_1(0)$ and static refraction index n(0) decrease. This may provide a possible way for finding

materials with appropriate static dielectric constants . The larger $\varepsilon_1(0)$ means a larger refractive index n(0). The respective theoretical values of $\varepsilon_1(0)$ are 5.49 and 9.47 corresponding to parallel and perpendicular directions to the *c-axis* for ZnO [22]. The agreement among them is good. While, The index of refraction was measured to be 2.35 along *c-axes* for ZnO [22] showing an excellent agreement with our calculated value.

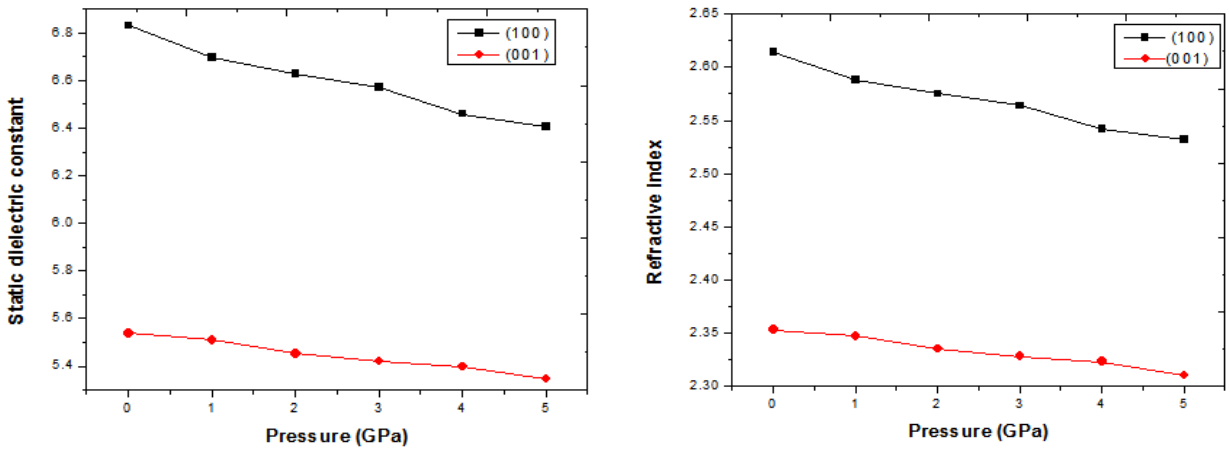

Fig.3. Static dielectric constant and refractive index as a function of pressure of ZnO.

3.4. Elastic properties

Elastic properties of a solid give important information on the mechanical and dynamical properties, such as inter-atomic potentials, equation of state and phonon spectra. The elastic constants are important parameters that describe the response to an applied macroscopic stress and especially important as they are related to various solid state phenomena, such as bonding characteristic between adjacent atomic planes, anisotropic character of binding and structural stability. The traditional mechanical stability conditions of the elastic constants in hexagonal crystal are known as to be [23-24] at 0 GPa:

$$C_{11} > 0, C_{11} - C_{12} > 0, C_{44} > 0, (C_{11} + C_{12})C_{33} - 2C_{13}^2 > 0 \qquad (3)$$

From the independent elastic constants above, the theoretical elastic modulus can be obtained. There are two approximation methods to calculate the modulus, namely the Voigt and Reuss method, as show in the equations (4, 5, 6, 7,8, 9):

$$G_V = \frac{1}{5}(2C_{11} + C_{33} - C_{12} - 2C_{13}) + \frac{1}{5}(2C_{44} + C_{66}) \quad (4)$$

$$B_V = \frac{2}{9}(C_{11} + C_{12} + 2C_{13} + C_{33}/2) \quad (5)$$

$$B_R = \frac{1}{2(S_{11} + S_{33}) + 2(S_{12} + 2S_{13})} \quad (6)$$

$$G_R = \frac{15}{4(2S_{11} + S_{33}) - 4(S_{12} + 2S_{13}) + 3(2S_{44} + S_{66})} \quad (7)$$

$$B_H = (1/2)(B_V + B_R) \quad (8)$$

$$G_H = (1/2)(G_V + G_R) \quad (9)$$

The Young's modulus (*E*) is then calculated from these elastic constants using the following equation:

$$E = \frac{9BG}{3B+G} \quad (10)$$

The obtained values of C_{11}, C_{12}, C_{13}, C_{33} and C_{44} at zero temperature and various pressures (up to 5 GPa) are shown in Table 2, and the relationships of elastic constants with pressures are shown in Fig. 4. As shown in Fig. 4, C_{11}, C_{33}, C_{12} and C_{13} increase with increase the pressure, however, C_{44} decreases with increase the pressure. The current results are in well agreement with previous experimental and other theoretical results.

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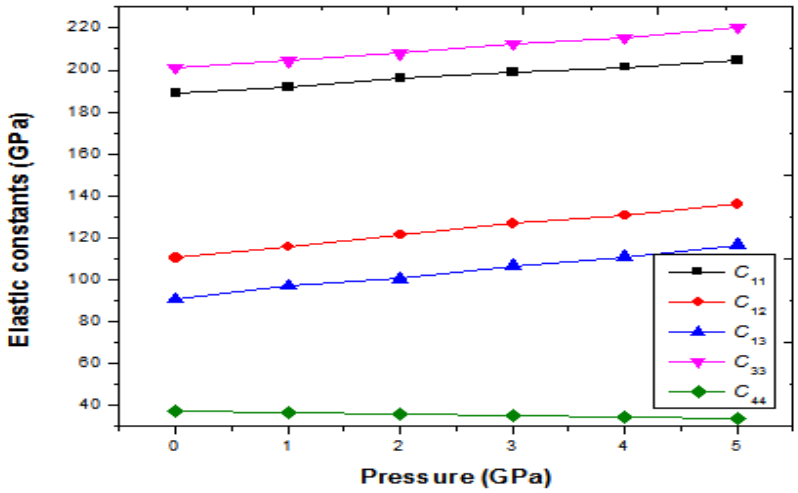

Fig.4. Variation of elastic constants with pressure of ZnO

The mechanical properties of ZnO as a function of pressure is shown in Fig. 5 and the values are listed in Table 2. From the figure and table can be seen, the Bulk modulus increases with the pressure increasing. however, Shear modulus and Young's modulus decrease with increase the pressure.

Table 2. The calculated elastic constants and mechanical properties of ZnO at 0 GPa.

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	B	G	E
	188.96	110.32	90.42	200.97	36.87	129.00	41.26	111.85
	209[a]	120[a]	104[a]	21[a]	44[a]	142[a]	44[b]	111.2[a]

[a] Ref.[25], [b] Ref.[26]

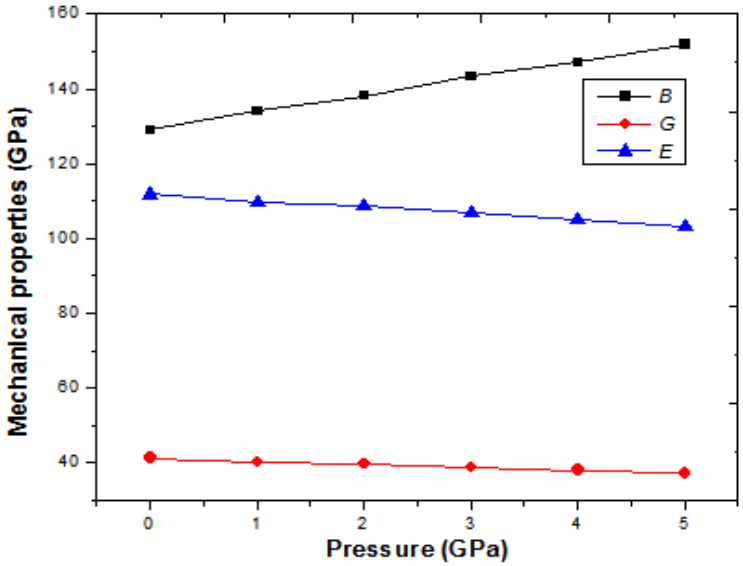

Fig.5. Mechanical properties as a function of pressure of ZnO.

The mechanical properties of ZnO as a function of pressure is shown in Fig. 5 and the values are listed in Table 2. From the figure and table can be seen, the Bulk modulus increases with the pressure increasing. however, Shear modulus and Young's modulus decrease with increase the pressure.

4. Conclusion

In summary, the electronic, optical, and elastic properties of ZnO as a function of pressure have been investigated using the first-principles calculations with the plane-wave ultra soft pseudo potential technique. The obtained lattice constants indicated a close agreement with the reported experimental values and literature data. It is noted that the band gaps increase with the pressure increasing. In addition, we can observed that the static dielectric constants $\varepsilon_1(0)$ and static refraction index n(0) decrease with the increasing pressure. The elastic constants (C_{11}, C_{33}, C_{12} and C_{13}) and the Bulk modulus *B* increase with the increasing pressure, however for C_{44}, shear modulus (G) and Young's modulus (E) decreases with the increasing pressure. According to stability criteria, ZnO is mechanically stable when the pressure varies from 0 to 5 GPa. It is clearly seen that our results are in excellent agreement with the experimental and previous theoretical ones.

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