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Study the Influence of High Pressure on the Optical and Electronic Properties of Composite ZnO Using (DFT-GGA)

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ABSTRACT

In this article, the lattice constants, band structure and optical characteristics of ZnO wurtzite structure under various pressures were studied using the generalized gradient approximation (GGA) method. This method is based on the functional density (DFT) Theory, according to the first principle. The results show that as the pressure increases and the band gap increases, the lattice constants (a and c) decrease. As the pressure increases, the minimum conduction band will move to a higher energy level, and the maximum valence band will move to a lower energy level, thereby increasing the energy band difference. As the pressure increases, the shape of the optical parameter curve remains almost unchanged, and all peaks move to higher energies. The state density, dielectric function, reflectance and absorption coefficient are also calculated. The overview of the spectrum and optical properties is discussed, including the imaginary part of the dielectric function, reflectance and absorption coefficient of wurtzite-type ZnO under environmental conditions. The optical constants indicate that the phase of ZnO wurtzite structure is transparent. We noticed that our measurements are comparable to those observed in the literature.

Keywords: Zinc oxide, functional density (DFT) theory- generalized gradient approximation, optical properties, electronic properties.

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INTRODUCTION

ZnO has been widely used because it can be used in many optical devices, such as electrochemistry, optoelectronics, water splitting (Li and Zhang, 2010), ultraviolet detectors (Liu *et al*., 2010), lasers (Kalusniak *et al*., 2009), optically transparent electrodes (Ellmer, 2012), transparent thin film transistors and Metal diode-insulation-semiconductor (Özgür *et al*., 2005). The ZnO and its compounds remain the dominant hot topic in functional materials due to their directness of a 3.37 eV energy gap at room temp, high binding energy of the 60 meV exciton, and corresponding applications (Reynolds *et al*., 1996; Bagnall *et al*., 1997). ZnO behavior under high pressure is also a very important topic in the fields of Physics with basic material (Jaffe *et al*., 2000). Zinc oxide is a naturally occurring metal oxide that exists in the form of minerals in the form of zincate. Generally used in the industry to produce rubber, concrete and paint (Kolodziejczak and Jesionowski, 2014). With the advancement of high-pressure experiments, a lot of ideas about the structure and the photoelectric properties of ZnO were discovered under pressure (Kolodziejczak and Jesionowski, 2014; Wang *et al*., 2013). Then it is not possible to avoid the original point defects in the ZnO growth process, the high-pressure properties are calculated because the pure ZnO material does not correspond to the current funding situation. Therefore, although there are a great number of experimental and theoretical publications on the characteristics of zinc oxide composite structures having vesicle impurities and pure of ZnO wurtzite structure high - pressure behavior (Wang *et al*., 2014; McCluskey and Jokela, 2009; Sun *et al*., 2013), our understanding of the structure, electrical and optical properties of ZnO will still be considered defects such as oxygen vacancies and interstitial zinc are limited and incomplete under high pressure. Using the full potential linear muffin-tin orbital (FP-LMTO) method (Andersen *et al*., 2001), the band structures of ZnO corresponding to different pressures are obtained. From Periodic functional density (DFT) theory calculations (Marana *et al*., 2017). Study the pressure-induced piezoelectric, elastic, infrared and Raman behaviors of ZnO wurtzite structure. Permanent densification of amorphous zinc oxide under pressure: first-principles analysis (Tahaoğlu and Durandurdu, 2018). Moreover, there are many works about ZnO structural, electrical and vibrational properties and performances as a function of pressure (Serrano and Romero,2004; Pellicer-Porres et al.,2011; Saitta and Decremps, 2004). However, there have been many studies. on the effect of pressure on elasticity, piezoelectricity, and dielectric constant. In this study, the DFT/GGA method was first used to examine the effect of variable pressure treatment on the structure of ZnO, and other optical properties were also calculated.

THEORETICAL PARTS

GENERALIZED GRADIENT APPROXIMATION (GGA)

The Local Density Approximation relied on the electron gas model and thus assumed a uniform electron density, other than atomic or molecular systems are very different from homogeneous electron gas, and in general we can consider that all real systems are heterogeneous, meaning that the electronic density varies locally. This is what led to the emergence of Generalized Gradient Approximation (GGA) which is also called the (non-local) method that depends only on the electronic density, but also on their gradient, and thanks to this modification the term energy was written as follows (Perdew *et al*.,1993):

$$E_{XC}^{GGA}[n] = \int dr^3 \varepsilon_{xc}[n(r), \nabla(n)] \qquad \ldots\ldots\ldots\ldots\ldots (1)$$

The GGA resolved the problem and failure of GEA of the exchange potential. Also overcome the problem of the over binding of Local Density Approximation which caused small lattice parameters.

SIMULATION

For calculations (Segall *et al*., 2002), the CASTEP code was used. And incorporated into the software of Materials Studio. The program is based on its work on the theory of functional density (DFT). Generalized Gradient Approximation (GGA) was chosen as the methodological basis for the density function (Chan and Ceder, 2010). This software was used to research the electronic structures of the ZnO system with considerable success (Yoshinari *et al*., 2009; Su *et al*., 2009). By optimizing all crystal atoms with ultra-soft pseudopotentials, the electronic structure was determined with the core electrons of basic electrons. The cut-off energy in the expansion of the plane wave is 380V. The overall energy is less than $2x10^{-6}$ eV.

CASTEP CODE

CASTEP (originally from Cambridge Serial Total Energy Package) is a shared-source academic and commercial software package which uses density functional theory with a plane wave basis set to calculate the electronic properties of crystalline solids, surfaces, molecules, liquids and amorphous materials from first principles. CASTEP permits geometry optimization and finite temperature molecular dynamics with implicit symmetry and geometry constraints, as well as calculation of a wide variety of derived properties of the electronic configuration. Although CASTEP was originally a serial, Fortran 77-based program, it was completely redesigned and rewritten from 1999 to 2001 using Fortran 95 and MPI for use on parallel computers by researchers at the Universities of York, Durham, St. Andrews, Cambridge and Rutherford Labs (Segall *et al*., 2002). A schematic representation of a self-consistent loop in this numerical method is depicted in Fig.1. (Woods *et al*., 2019).

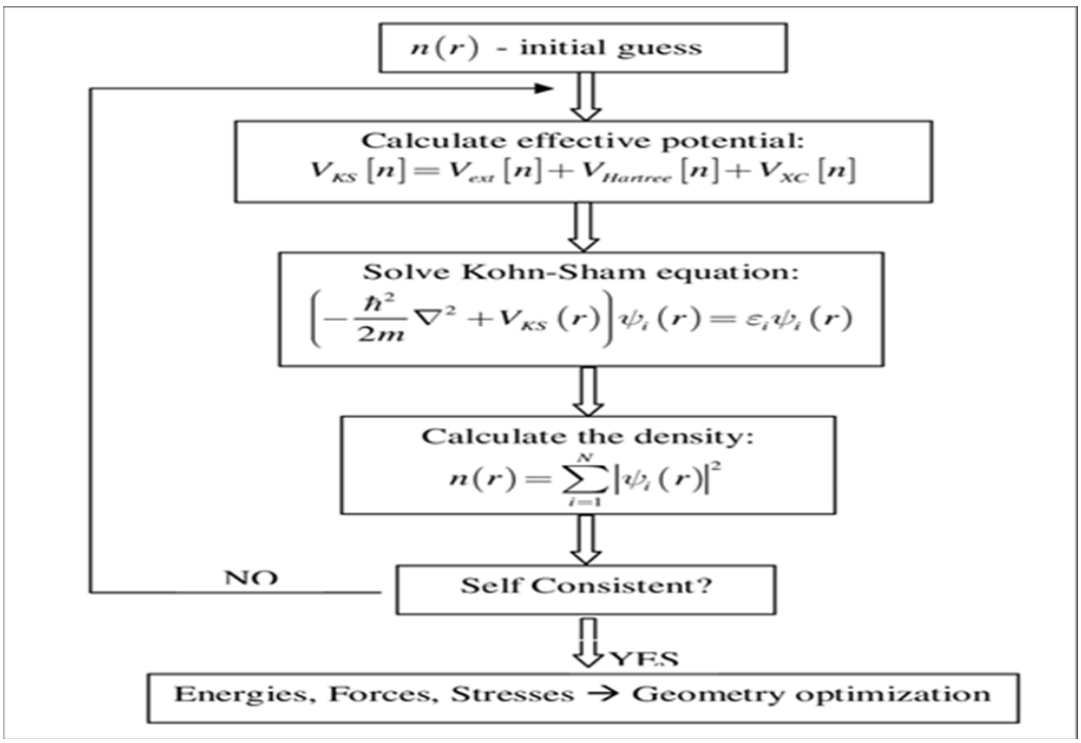

Fig. 1: Flowchart of self-consistent Kohn-Sham calculation

RESULTS AND DISCUSSIONS

The optimized parameters of the cell constant (a and c) are in good agreement with the available experimental data, (Decremps *et al*., 2003) are also reported in Table 1. It is worth noting that at room temperature, a transition phase of ZnO wurtzite structure to rock salt ZnO is observed about 9 GPa. (Pellicer-Porres *et al*., 2011) However, the stable stage of rock salt is as high as 56.6 GPa (Desgreniers, 1998). Hence, various pressures starting 0 in 30 GPa (P = 0.0, 6, 12, 18, 24, 30

GPa) are applied to the optimized zero-pressure structure, and each pressure is subjected to geometric relaxation of symmetrical constraints. Determine the energy gap and lattice constant of each equilibrium geometry under pressure. (Table 1) summarizes the results of structural parameters, volume and band gap energy, In the same table, his work results were compared with the previous results (Decremps *et al*., 2003; Bornstein *et al*., 1979; Zhao *et al*., 2014; John and Padmavathi, 2016), we noticed that a good agreement were noticed with their results except for the energy gap. The theoretical and experimental results are different, it is well known that GGA do not accurate depict the valence band position because of the loose treatment of correlation. Fig. (2), shows the linear relationship between various parameter c, a and volume and pressure. This indicates structural properties decrease with linearly with increasing pressure. In Fig. (3a) the energy band gap of ZnO wurtzite structure using GGA-PW91 is 0.75eV, closed to the other DFT calculation, then much lesser than the experimental worth (3.37eV) that due to the shortcoming of self-interaction inherent in GGA functional for strongly correlated electron systems with localized electrons. The band gap of ZnO wurtzite structure with hydrostatic pressure is shown in Fig. (3b). In addition, the energy band gap broadens with increasing pressure, which is similar to the result found in (Zhao *et al*., 2014). The band gap/pressure relationship can generally be described as:

$$E_g(p) = a + b\,p \qquad \text{……………………………….. (2)}$$

Where Eg in (eV) and P in (GPa) are the energy band gap and pressure respectively, a and b are constants. When the fitting pressure is between (0 – 30) GPa. The fitting equation is $E_g(p) = 0.762 + 0.0074P$. This formula can be used to identify of ZnO wurtzite structure and measure pressure after careful calibration.

Table 1: Structural parameters, volume and gap energy various pressure of ZnO wurtzite structure using GGA-PW91 compared with both experimental and theoretical data reported in the (Decremps *et al*., 2003; Bornstein *et al*., 1979; Zhao *et al*., 2014; John and Padmavathi, 2016) literature.

Method	Pressure (Gpa)	Lattice parameter(A^0)		$V(A^0)^3$	Eg (eV)
		a	c		
Present work Using GGA- pw91	0	3.2788	5.2934	49.283	0.75
	6	3.2328	5.2203	47.250	0.81
	12	3.1948	5.1594	45.607	0.86
	18	3.1617	5.1072	44.215	0.903
	24	3.1327	5.0628	43.029	0.939
	30	3.1090	5.0150	41.982	0.974
Experimental (Decremps *et al*., 2003[a]; Bornstein *et al*., 1979[b])	0	3.26[a]	5.22[a]	47.98[a]	3.37[b]
GGA-PBE (Zhao *et al*., 2014)	0	3.315	5.3425	50.881	0.437
	2	3.31	5.33	50.419	0.4659
	4	3.28	5.30	49.362	0.468
	6	3.265	5.27	48.682	0.480
	8	3.25	5.25	48.053	0.490
mBJLDA (John and Padmavathi, 2016)	0	3.286	5.269	49.354	2.683

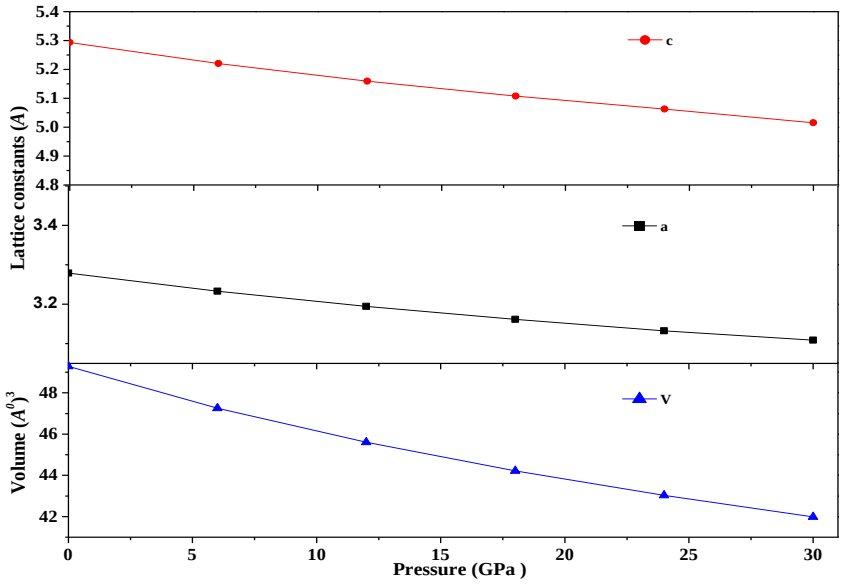

Fig. 2: Lattice parameter c, a and volume of ZnO wurtzite structure under different pressures using GGA-PW91

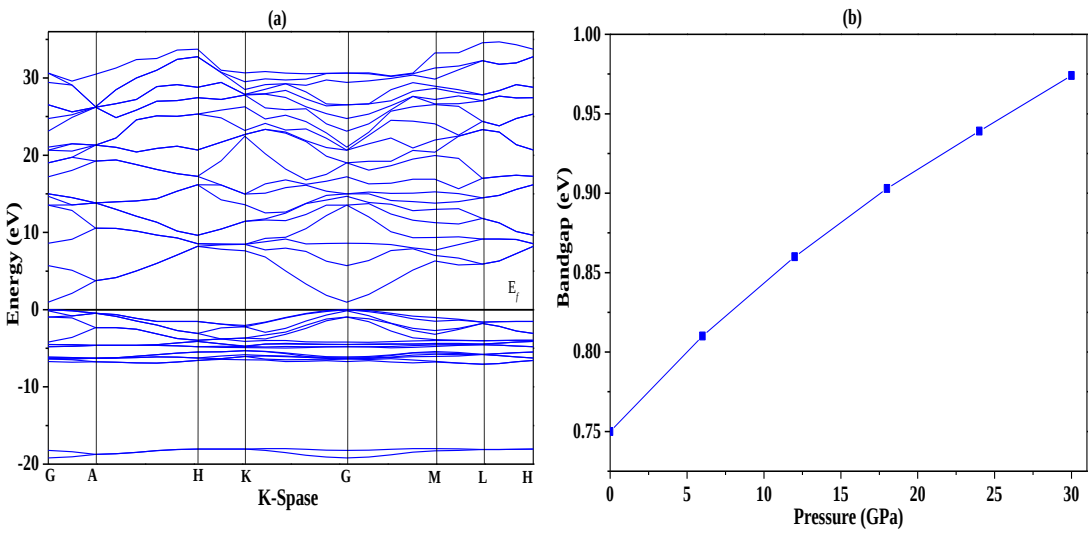

Fig. 3: ZnO wurtzite structure (a) band structure at zero pressure and (b) band gap versus pressure using GGA-PW91

At the same time, Fig. (4) explains the changes of the TDOS curve relative to the pressures of 0, 6, 12, 18, 24, and 30 GPa. The results show that the maximum energy of the valence band increases from these changing curves as the applied pressure increases, while one of the bottoms of the conduction band has been reversed, which means that the high pressure reduces the band gap between the conduction band and the valence band, and the external electrons seem to be easily transferred from the maximum valence band to the bottom of the conduction band. Therefore, high pressure may destroy the structural stability of ZnO wurtzite structure, thereby affecting the microstructure and microphysical properties of zinc oxide. The TDOS value of the Fermi level will become smaller, and as the pressure increases, the energy region close to the Fermi level will also widen. Under all stress conditions, as the energy increases, the TDOS value obtained at the Fermi level decreases to zero, and then gradually increases. In Additionally, we can also notice that the TDOS peaks are moving to the low energy region. This may be due of the smaller distance of the compressed atoms, which leads in having to change potential interactions.

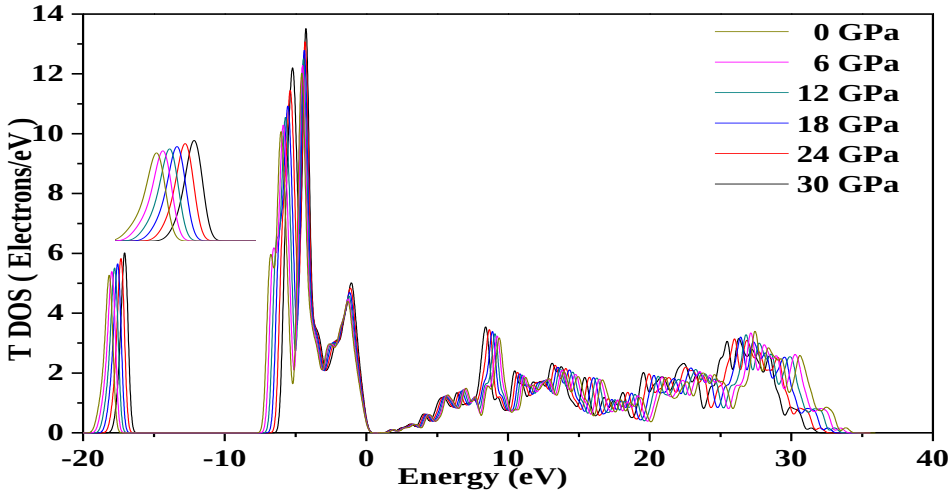

Fig. 4: Total density of state via different pressures of ZnO wurtzite structure using GGA-PW91

Fig. (5) (a and b) Show the state density of each valence band and conduction band shifts to low energy and high energy, respectively. When the pressure increases from 0 GPa to 30 GPa, the width of the valence band increases slightly, while the relative strength decreases slightly. The larger the gap between the Fermi surface and the energy band, the greater the movement of the energy band under pressure. When the valence band and the conduction band move in opposite directions, the band gap widens significantly. Whenever the pressure is increased to 30 GPa, that band gap widens significantly as well as the conduction band shifts toward high energy. Under the pressure of 2GPa, 6GPa and 8GPa, the DOS is different. This may be due to the transformation of of ZnO wurtzite structure.

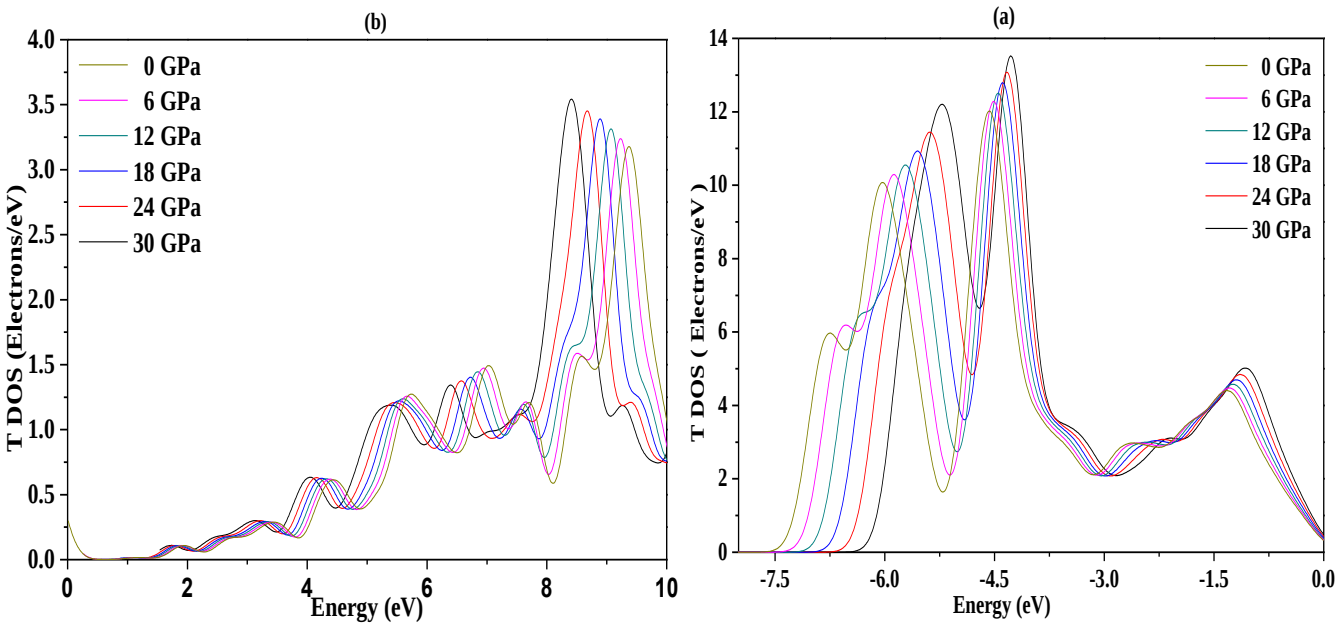

Fig. 5: Total density of state of wurtzite ZnO under various pressures: (a) Valence band, (b) Conductive local band

The relationship between the imaginary part of the dielectric function and energy under various pressure is indicated in Fig. (6). As the pressure increases, the ε2 curve remains basically unchanged, and those peaks move to higher energy levels. Since the origin in k- space remains unchanged under static pressure, it is believed that the shift to the higher energy peak is caused by the increase in the energy of the critical point. An important quantity is the imaginary dielectric function; it describes the two interbond transitions between the bands of valence and conduction. From the feature of the imaginary part ε2 displayed in Fig. (7), there are four groups of peaks of ZnO wurtzite structure over a range of photon energies up to 50 eV. From first peak to the four peak (2-3) eV, (7-8.5) eV, (11-12.5) eV and (13-14) eV photon energy, respectively for different pressure (0 – 30) PGa. The first and third peaks come from direct optical transitions of electrons among Zn-4s and O-2p and between O-2s and Zn-3d states, respectively. These four peaks might have been the result of an electronic transition as between the O-2p and Zn-3d states (Adachi, 2013). Fig. (7) (a and b) displays the absorption and reflection spectra of ZnO wurtzite structure. The results indicate that as the pressure increases from (6 to 12) GPa, the absorption edge and all absorption peaks shift to the high energy direction (short wavelength). Since the band gap between the valence band and the conduction band increases as pressure is increased. Consequently, the 2p electrons of oxygen jump into the valence band, and more energy is needed to achieve this. When the pressure rises to 30 GPa, the absorption edge will obviously move in the direction of high energy, and the shape of the absorption curve will change. From the absorption spectrum of figure 7a, we can see that the basic absorption edge of ZnO wurtzite structure attenuates with the increase of pressure. On the other hand, there are two main peaks (regions), one between 11 and 17 eV and the other between 30 and 40 eV. Optical absorption mainly originates from the excitation of inter-band electrons between the valence band and the conduction band. All absorption peaks can correspond to the (ε2) peaks of GGA-pw91 in of ZnO wurtzite structure derived from the same electronic transition. E.g., From the direct electronic transition from the *O-2p* state in the valence band to the *Zn-4s* state in the conduction band, the first absorption peak corresponding to the first peak of the (ε2) spectrum is derived. As shown in the figure 6b, Reflectance spectrum of zinc oxide from zero pressure to 30 pressure. The zero-frequency reflectivity R (0) of ZnO wurtzite structure is 15%-17.5%. The figure shows that under the same pressure, the highest reflectance range in the range of 15-16 eV is 38% [32].

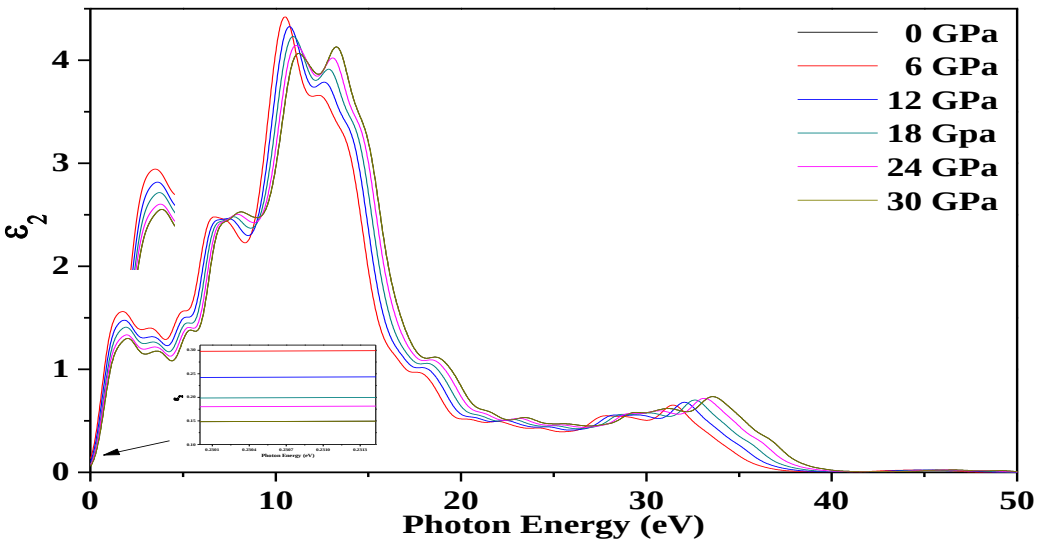

Fig. 5: The imaginary dielectric part of ZnO at different pressures using GGA-PW91

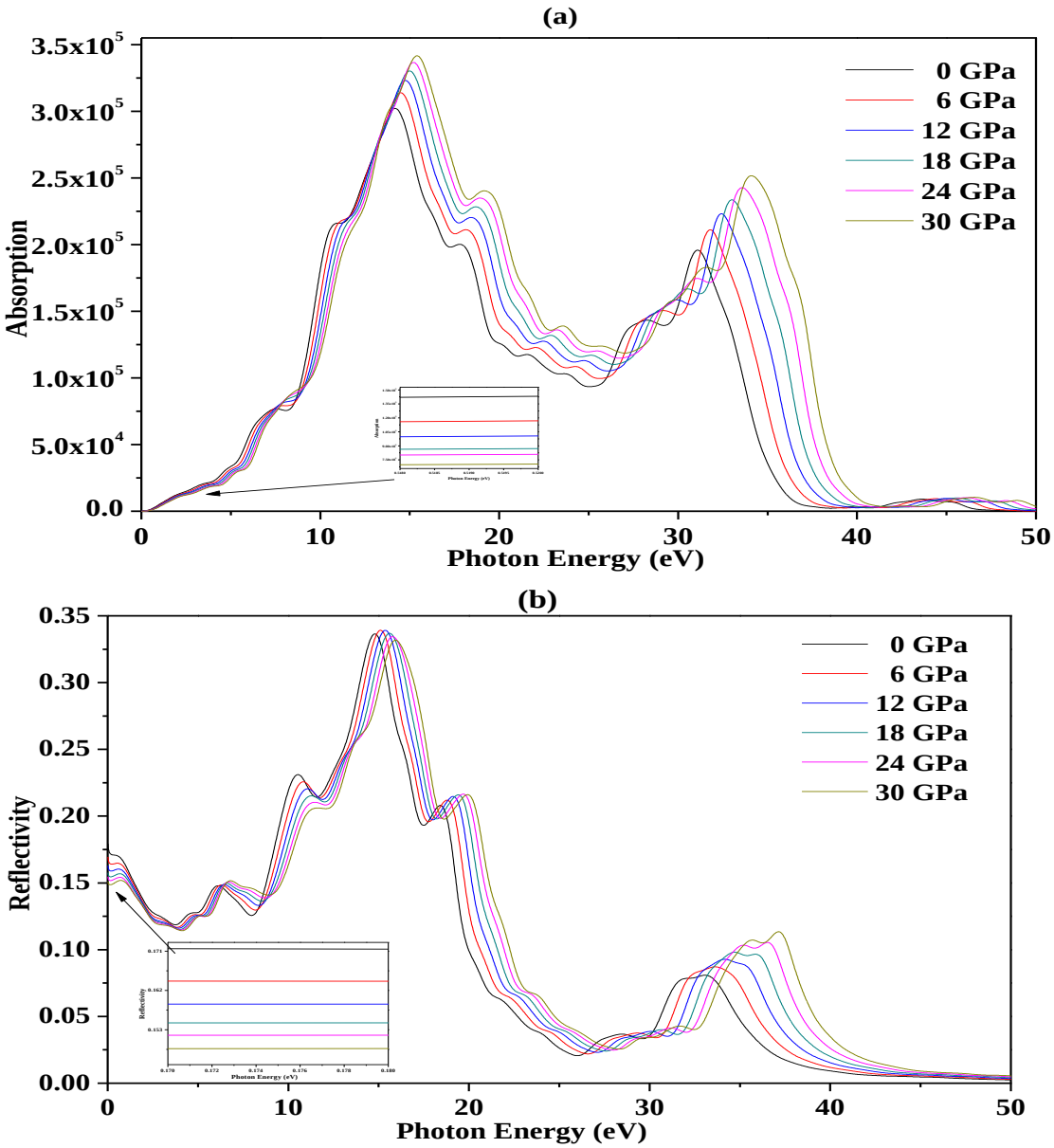

Fig. 7: Calculated: (a) absorption coefficient and (b) reflectivity under high pressures using GGA-PW91

CONCLUSIONS

The structural, electronic and optical characteristics of ZnO wurtzite structure were investigated under normal and different pressures using first-principal calculations using the theory functional density and the general gradient approximation of the plane norm conserved pseudo - potential. That results indicate that as pressure increases, the lattice constants (a and c) of ZnO decrease, but the band gap increases because CBM moves to higher energy and thus VBM moves to lower energy. Under increasing pressure, the dielectric constant ε1(0) and the refractive index n (0) decrease monotonously. Since the pressure increases, the shape of the optical parameters ε2(ω), α(ω) and n(ω) remains nearly unchanged, however all of the peaks shift to higher energy.

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دراسـة تأثير الضغط العالي على الخصائص البصرية والإلكترونية لمركب اوكسيد الزنك باستخدام (DFT-GGA)

الملخص

في هذه المقالة، تمت دراسة الثوابت الشبيكة، وتركيب الحزمي، والخصائص البصرية لـ الزنك اوكسيد تحت ضغوط مختلفة باستخدام أسلوب تقريب التدرج المعمم. تعتمد هذه الطريقة على نظرية الكثافة الوظيفية وفقا للمبدأ الأول. وتظهر النتائج أنه كلـما زاد الضغط تزداد فـجوة الطـاقة، وتنخفض ثوابت الشبيكة (a و c). ومع زيادة الضغط، سينتقل الحد الأدنى لحزمة التوصيل إلى مستوى طاقة أعلى، وستتحرك حزمة الحد الأقصى للتكافؤ إلى مستوى طاقة أقل، مما يزيد الفرق في حزمة الطاقة. ومع زيادة الضغط، يظل شكل منحنى المعامل البصرية دون تغيير تقريبا، وتنتقل كل القمم إلى طاقات أعلى. كما يتم حساب كثافة الحالة ودالة العزل الكهربية ومعامل الانعكاس والامتصاص. حيث تم مناقشة طيف والخصائص البصرية، بما في ذلك الجزء الخيالي من الدالة العازلة، ومعامل الانعكاس والامتصاص من نوع ZnO Wurtzite في ظل الظروف البيئية. واظهرت الثوابت البصرية على أن اوكسيد الزنك شفافة. قورنت نتائج هذا العمل النظرية مع النتائج العملية لمصادر سابقة وكانت متوافقة معها.

الكلمات الدالة: أوكسيد الزنك، نظرية الكثافة الوظيفية (DFT) – تقريب التدرج المعمم، الخصائص البصرية، الخصائص الإلكترونية.