Ab initio study of mechanical, phonon and electronic Properties of cubic zinc-blende structure of ZnO

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Abstract
The search for functional materials in opto-electronic devices is a major aspect of material research in contemporary times and a meta-stable structure of ZnO has been proposed as one such relevant materials. Herein the elastic constants, lattice dynamical and electronic properties of the cubic zinc-blende ZnO (ZB-ZnO) were studied at ambient pressure using the density functional theory method within the generalized gradient approximation. The result shows that ZB-ZnO is mechanically and dynamically stable, ductile and a direct band gap semiconductor and is very promising for opto-electronic applications. The results are in fair agreement with the available data in the literature.

Keywords: ZnO; density functional theory; phonon; elastic constant; electronic structure.

Introduction

Recent research results have stressed that II-VI semiconducting compounds are very promising in technological applications (Chibueze and Okoye, 2019). Among them is Zinc (II) oxide (ZnO) which has generally received tremendous attention in the last few decades in the literature (Ding, Wang, Sun and Qiu, 2007; Haq et al 2020; Baranov *et al*, 2013; Ashrafi and Jagadish, 2007). ZnO has three major polymorphs: wurtzite, zinc-blende and rock-salt structures (Ashrafi and Jagadish, 2007). The wurtzite structure has a wide band gap and is therefore popularly used as transparent material in solar cells (Harun, Salleh, Deghfel, Yaakob and Mohamad, 2020). It has been reported that ZnO transits from the wurtzite structure to rock-salt structure at pressure of about 9.0 GPa and the rock-salt structure is a small band gap semiconductor relative to the wurtzite (Segura, Sans, Manjon, Munoz and Herrera-Cabrera, 2003). Cubic zinc-blende ZnO has been demonstrated both experimentally and theoretically to be a metastable phase of ZnO. Although the wurtzite structure ZnO has often been reported in experiments, a few cubic zinc-blende structure of ZnO has been synthesized a few times under ambient condition (Ashrafi and Jagadish (2007)). For example, cubic zinc-blende ZnO has been synthesized by Ashrafi et al (2000) using the method of molecular beam epitaxy. Also, cubic zinc blende ZnO thin films have been grown on glass substrates using the spray pyrolysis technique by Muñoz-Aguirre *et al* (2019). Zhou *et al* (2008) synthesized single crystalline cubic zinc-blende ZnO nano rod array with rectangular cross-section. Chichvarina et al (2015), fabricated the stable zinc-blende ZnO on Pt/Ti/SiO2/Si substrate via phase transformation from the originally wurtzite to the zinc-blende phase. This is because there is close relation between the wurtzite and zinc-blende structures which includes that they both have similar packing fraction of ~75%. However, there appears to be conflicting reports on the nature and size of the band gap of cubic zinc-blende ZnO despite its promising properties. In light of these, there is need for detailed understanding of the origin of the variations in the electronic properties of the zinc-blende ZnO reported in the literature which is a major role of theoretical material science. Moreover, the study will give a measure of accuracy of the results on properties of binary transition metal oxides such as ZnO obtained using revised PBE functional relative to other exchange-correlation functional.

In the present study, the dynamical, mechanical and electronic properties of the cubic zinc-blende ZnO have been examined and the results have been compared with existing reports in the literature. In section 2, the computational details is outlined. In section 3, the results is presented and discussed while section 4 is the conclusion.

Theoretical Methods

Density functional theory (DFT) (Hohenberg and Kohn, 1964) spin polarized calculations have been performed within the generalized gradient approximation (GGA) with revised Perdew, Burke and Ernzerhof exchange-correlation functional (PBEsol) by Perdew *et al* (2008). The Kohn-Sham equation (Kohn and Sham, 1965)

$[-\frac{1}{2}\nabla^2+V_{ext}+V_H(r)+V_{xc}(r)]\phi_i(r)=\epsilon_i\phi_i(r)$ (1)

was solved using the variational principle. In the Kohn-Sham equation, $-\frac{1}{2}\nabla^2$ is the quantum kinetic energy of the electrons, V_{ext} is the external potential created by the ions, $V_H(r)$ is the Hartree potential given by

$$V_H(r)=\int d^3r'\frac{\rho(r')}{|r-r'|}. \quad (2)$$

$V_{xc}(r)$ is the exchange-correlation potential given by

$$V_{xc}(r)=\frac{\delta E_{xc}[\rho(r)]}{\delta\rho(r)}, \quad (3)$$

where,

$$E_{xc}^{GGA}[\rho(r)]=\int d^3rf[\rho(r),\nabla\rho(r)]=E_x^{GGA}[\rho(r)]+E_c^{GGA}[\rho(r)]\ . \quad (4)$$

Plane-wave self-consistent field (PWSCF) method have been employed, as implemented in the Quantum-Espresso program package of Giannozi et al, (2009) in the calculations. Kinetic energy and augmented charge density cutoff of 80 Ry and 240 Ry were used respectively. At this cutoff, the total energy is converged to within 1 mRy/atom. Scalar relativistic norm-conserving pseudopotentials of Hamann et al (1979) were used to describe the interaction between ions and

ϵ_i is the energy eigenvalue and ϕ_i is the Kohn-Sham orbital.

valence electrons. Zn 1s, 2p,3d, 4s and O 1s, 2p are treated as valence orbitals. Brillouin zone integration was done over 12 x 12 x 12 k-point grid sampled by Monkhorst-Pack scheme (Monkhorst and Pack, 1976). The optimization criteria for the ionic geometry relaxation was 0.0001 Ry for total energy and 0.001Ry/au for the Hellmann-Feynman forces. In order to calculate the phonons and electronic band structure, the Coulomb repulsion term U_{eff} was added to the PBEsol functional using rotationally invariant procedure proposed by Dudarev, Botton, Savrasov, Humphreys and Sutton (1998). U_{eff} of 4.15 eV on the Zn d orbital. Using the optimized geometric structure, the phonons, elastic constants, mechanical and electronic properties of cubic zinc-blend ZnO was examined using the primitive unit cell containing one Zn and one O atoms (see Figure 1).

Result and Discussion

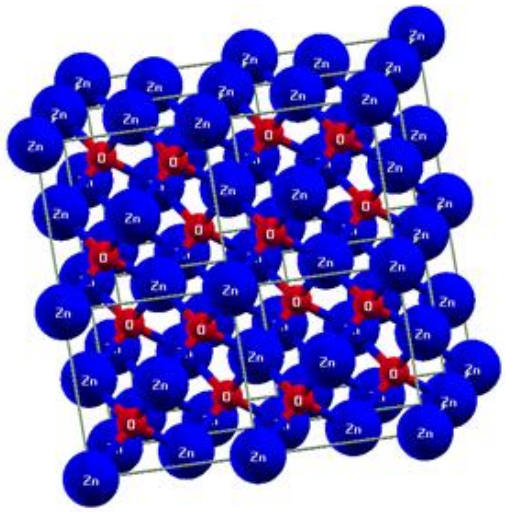

Figure 1: Crystal structure of cubic zinc-blende ZnO. The blue atoms are the zinc while the red atoms are the oxygen. We have used 2x2x2 unit cell so as to see the bonding arrangements.

Mechanical properties: Elastic constants are used to obtain the mechanical properties of a material. The tensor C_{ij} decides the elastic property of the material. For any cubic structure, there are three components C_{11}, C_{12} and C_{44} of the elastic constant tensor needed in order to determine the mechanical stability. In order to confirm mechanical stability of a material, the Born and Huang (1954) stability criteria must be satisfied. These conditions are:

$$C_{11}, C_{44}>0, C_{12} < B < C_{11}, C_{11}-C_{12} > 0, \quad C_{11}+2C_{12} > 0 . \quad (5)$$

Compressibility is measured using the bulk modulus B which is a measure of resistance to volume change on application of pressure given as

$$B=\frac{C_{11}+2C_{12}}{3}. \quad (6)$$

Stiffness of a material is measured using the shear modulus G which is a measure of resistance to reversible deformation upon shear stress. G is obtained using three different approximations:
The Voigt (1928) approximation given by

$$G_V = \frac{C_{11}-C_{12}+3C_{44}}{5}, \quad (7)$$

the Reuss (1929) approximation given by

$$G_R = \frac{5C_{44}(C_{11}-C_{12})}{4C_{11}+3(C_{11}-C_{12})}, \quad (8)$$

and the Voigt-Reuss_Hill (1952) approximation which is average of the first two and is given by

$$G=\frac{G_V+G_R}{2} \quad (9)$$

Young Modulus, a ratio of the linear stress to strain, which is another measure of stiffness is given by

$$E\frac{9BG}{3G-B} . \quad (10)$$

Another important quantity is the Poisson's ratio υ which is given by

$$\upsilon=\frac{3B-2G}{2(3B+G)} \quad (11)$$

For ductile materials $\upsilon=\frac{1}{3}$ while for brittle material $\upsilon<\frac{1}{3}$. Zener anisotropy factor A is given by

$$A=\frac{2C_{44}}{C_{11}-C_{12}} \quad (12)$$

The ratio $\frac{B}{G}$ is also used to determine if a material is brittle or ductile. A material is ductile if $\frac{B}{G} > 1.75$ and brittle if $\frac{B}{G} \leq 1.75$.

Using our optimized structure, we calculated the elastic properties and calculated the mechanical properties using a combination of Voigt and Reuss approximation called Voigt-Reuss-Hill (VRH) approximation. Our result for mechanical properties is shown in Table 1 and it shows that the Born stability criteria is satisfied confirming that cubic zinc-blende ZnO is mechanically stable. Our result for the elastic constants and and bulk modulus is in fair agreement but slightly higher in comparison with the results of Kalay *et al.*, (2009) and Serrano *et*

al., (2004) who used ordinary PBE exchange correlation functional (see Table 1). Also, it is clear from the values of υ and B/G ratio that the cubic zinc-blende of ZnO is very ductile. Unfortunately, we could not find any data to compare our result for υ and B/G ratio.

Table 1: The lattice constant, elastic constants, mechanical properties and band gap of cubic zinc-blende ZnO

A (Å)	C_{11}(GPa)	C_{12} (GPa)	C_{44} (GPa)	A	B (GPa)	E (GPa)	G (GPa)	υ	B/G	Direct band gap	Reference
4.55	171.30	149.37	72.6	6.62	156.68	97.26	35.15	0.38	4.46	1.36	Present study
4.58											Zhou *et al* (2008)
										3.06	Gerosa (2015)
										3.34	Huang (2001)
4.627					131.6					0.64	Schleife (2006)
4.504					160.8						Serrano (2004)
4.62											Oshikiri (1999)
	167.363	125.30	112.9								Kalay (2009)
										1.154	Yaakob (2014)

Phonon properties

Phonon calculations has been performed on cubic zinc-blende ZnO in order to understand the lattice dynamical properties. The phonon dispersion curves along the high symmetry directions together with the phonon density of states (PHDOS) are shown in Figure 2, where the longitudinal acoustical (LA), longitudinal optical (LO), transverse acoustical (TA) and transverse optical (TO) phonon modes have been clearly identified. Since two atoms were used in our unit cell, total of six phonon modes were obtained, three being acoustic and the remaining three optical. There are no negative frequencies observed which confirms that the cubic zinc-blende ZnO is dynamically stable and confirms the experimental claims of synthesizability. At the center of the Brillouin zone (Γ), LA and TA are zero and increase quardratically as one moves away from the zone center. Interestingly, LO and TO are degenerate at the zone center at frequency of 379 cm^{-1}. This is contrary to the result obtained by Yu et al., (2009) in which the LO and TO are distinct at Γ point with frequency of 517 and 367 cm^{-1} respectively. The disparity in the results comes from the fact that we have used an improved PBE functional which has been proven to work better for solids while they have used the ordinary PBE functional. At the symmetry point X, the frequencies of LA, TA, LO and TO are respectively 223, {93, 144}, 523 and {418,466} all in cm^{-1} unit. Yu el at., (2009) obtained 270, 121, 495 and 442 cm^{-1} respectively while Serrano et al, (2004) obtained 269, 128, 551 and 487 cm^{-1} respectively at LA, TA, LO and TO symmetry points and all the results are fairly comparable. At the symmetry point K, the frequencies of LA, TA, LO and TO are respectively 243, {103,135}, 453 and {429,459} all in cm^{-1} unit while at the symmetry point L, the frequencies of LA, TA, LO and TO are respectively 257, 90, 536 and 417 all in cm^{-1} unit. There is a wide phonon band gap between the longitudinal and acoustical phonon modes which also points to the semi-conducting nature of the compound.

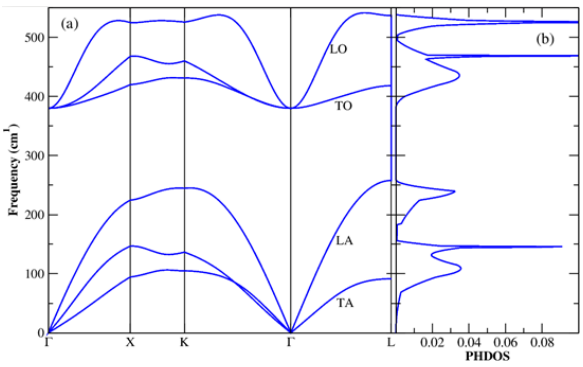

Figure 2: (a) Phonon frequencies or energy dispersion (b) Phonon density of states of cubic zinc-blende ZnO.

Electronic properties

The electronic structure of cubic zinc-blende ZnO has been calculated using the band structure and density of states. The results, recorded in Table 1 and Figure 3 show that the material is a direct band gap semiconductor with both the top of the valence band and the bottom of the conduction band occurring at the Γ point. The size of the band gap is 1.36 eV. Our band gap is

not comparable with the result of Harun et al (2020) obtained using GW approximation and the result of Huang et al (2001) obtained using UV-VIS spectroscopy. The result however is comparable with the result of Yaakob *et al* (2014). It is also observed that the top of the valence band is twofold degenerate while the bottom of the conduction band is a singlet states. In order to gain deeper insight into which states dominates around the Fermi level, the density of states projected on the atomic orbitals (PDOS) was calculated (see Figure 4). We observe from the PDOS that the top of the valence band is dominated by the O-2p states with little presence of the Zn-3d states with the Fermi level on top of the valence band. The bottom of the conduction band is dominated by the O-1s and Zn-4s states.

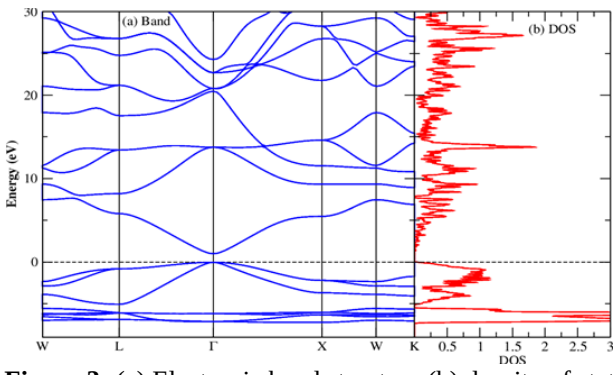

Figure 3: (a) Electronic band structure (b) density of states of cubic zinc-blende ZnO

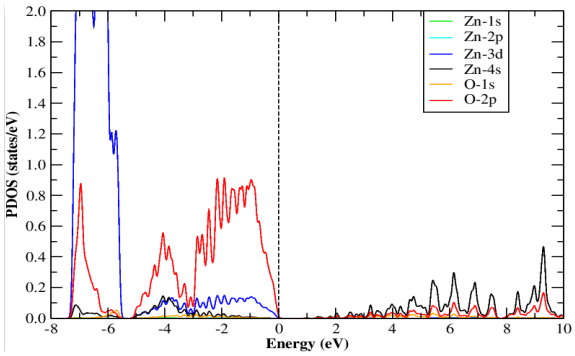

Figure 4: Electronic density of states projected on the atomic orbitals of cubic zinc-blende ZnO

Conclusion

In conclusion, the mechanical, phonon and electronic properties of cubic zinc-blende ZnO have been studied. The result shows that the ZnO is very ductile and both mechanically and dynamically stable. The electronic structure of the ZnO shows that it is fundamentally a direct band gap with possible direct transition at Γ point. These results are fair agreement with previous reports in literature and suggests that the cubic zinc-blende ZnO is promising as energy harvester in opto-electronic devices.

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