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THE INFLUENCE OF NITROGEN DOPING ON THE STRUCTURAL AND ELECTRONIC PROPERTIES OF ZINC OXIDE: A FIRST PRINCIPLE APPROACH

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Abstract

The structural and electronic properties of pure and nitrogen doped zinc oxide (ZnO) were studied using density functional theory (DFT) approach. The geometric optimization calculation showed that for the $ZnO_{1-x}N_x$ (x = 0, x = 0.125, x = 0.25 and x = 0.375), there is only minor increase in the lattice constants and therefore ZnO suffers less distortion on its structure, but the material loses its stability as the doping concentration is increased due to the increases in its formation energy. However, the band structure calculation described ZnO as a direct band gap semiconductor with its CBM and VBM lying on the same high symmetry Γ point with band gap energy of 0.79 eV. Our result also showed that insertion of 12.5% nitrogen impurity reduced the band gap of the material but enlarged when the dopant concentration was increased to 25% and also widened more for 37.5% doping concentration possibly due to Burstein Moss effect (BM-shift.

KEYWORDS: Density Functional Theory, Electronic Properties, Nitrogen, Zinc Oxide.

1. Introduction

Zinc oxide (ZnO) is an n-type semiconductor that has a wide direct band gap of about 3.37 eV at room temperature with exciton binding energy of 60 meV at 300 K (Rusu et al., 201) which is much larger compared to the room temperature thermal energy (26 meV). This binding energy has a significant influence on the electrical conductivity of a material (Iftime, 2014). ZnO bulk single crystals are among the qualities that make ZnO more advantageous over its counterpart GaN (Özgur, 2005).

However, the captivating and unique physical and chemical properties of ZnO such as wide band gap, good transparency, high electron mobility and strong room temperature luminescence, coupled with its numerous industrial applications are some of the qualities that make it the most studied material among the group II-VI compound semiconductors. It is considered to be a multifunctional compound ionic and covalent semiconductor (Jesionowski, 2014). ZnO appears in three different structural phases: high pressure rock salt (B1), room temperature stable wurtzite (B4) and Zinc blende (B3).

Moreover, for number of years now, researchers have shown significant interest in the study of ZnO (both bulk and nanocluster) properties due to its potentialities as a suitable solar cell material, thermoelectric materials, spintronic device (Qin, 2016). To have more diverse applications and potentialities, the need for devising means of increasing the conductivity of the ZnO arose. Doping is one of best way of achieving this, thus many elements have been selected as the dopants to obtain a more stable p-type ZnO Semiconductor, such as N , P, As, Sb, Cu, Li, Na, Ag and Au (Xuesi, 2016). While others like B, Al, Ga, In F and H produce n-type semiconductor.

Furthermore, nitrogen is considered to be the most suitable p-type dopant among the acceptor impurities that substitute oxygen due to its closeness in atomic size, electronic structure and electronegativity to that of oxygen (Walle, 2009). The Nitrogen ZnO dopants can be either interstitial or subtitutional at the Oxygen site. However, most of the works reported using nitrogen dopant are experimental based, the theoretical works are very rare.

Therefore, the aim of this work is to investigate the influence of nitrogen doping on the structural and electronic properties of zinc oxide using first principle study within the framework of Density Functional Theory (DFT).

2. Computational Method

In this work, the structural and electronic properties of pure and nitrogen doped Zinc Oxide (ZnO) were theoretically investigated using density functional theory (DFT) as implemented in the QUANTUM ESPRESSO simulation package (Giannozi et al 2009). The generalized gradient approximation (GGA) parametarization of Perdew-burke-ernzerhof (PBE) (Perdew et al., 1996) exchange-correlation (XC) scheme has been used for both the pure and doped ZnO. The Ultra-soft Pseudo potential (USP) is also used for the treatment of the electron-ion core interaction. The respective valence electronic configurations used for the construction are $3d^{10}4s^2$, $2s^22p^4$ and $2s^22p^3$ for Zn, O and N respectively. A convergence test was first performed on the tetragonal structure with space group $P4_2/mnm[136]$, the structure was fully relaxed until the forces on all the atoms are less than 0.82 eV/nm. The 200 Ry kinetic energy cut-off was used in the expansion of the wave functions and the k-points in the Brillouin zone were set to be $6 \times 6 \times 6$. However, the supercell used contains 8 atoms. Thus, three doping levels were considered in the calculations, first is $ZnN_{0.125}O_{0.875}$, with one N atom substituting a single O atom (which corresponds to 12.5% doping), followed by $ZnN_{0.25}O_{0.75}$, with two N atoms substituting two O atoms (which corresponds to 25% doping) and lastly $ZnN_{0.375}O_{0.635}$ (which corresponds to 37.5%).

3. Results and Discussions

3.1 Structural properties

For the optimized structure of the pure ZnO, our calculated values for the lattice constants are $a = b = 5.529$Å, and $c = 3.258$Å. These values are in good agreement with other experimental data like $a = b = 5.209$Å and $c = 3.253$Å (Shirsat, 2015) as well as theoretical results of $a = b = 5.206$ Å and $c =$ 3.2496 Å according to (Franklin, 2013).

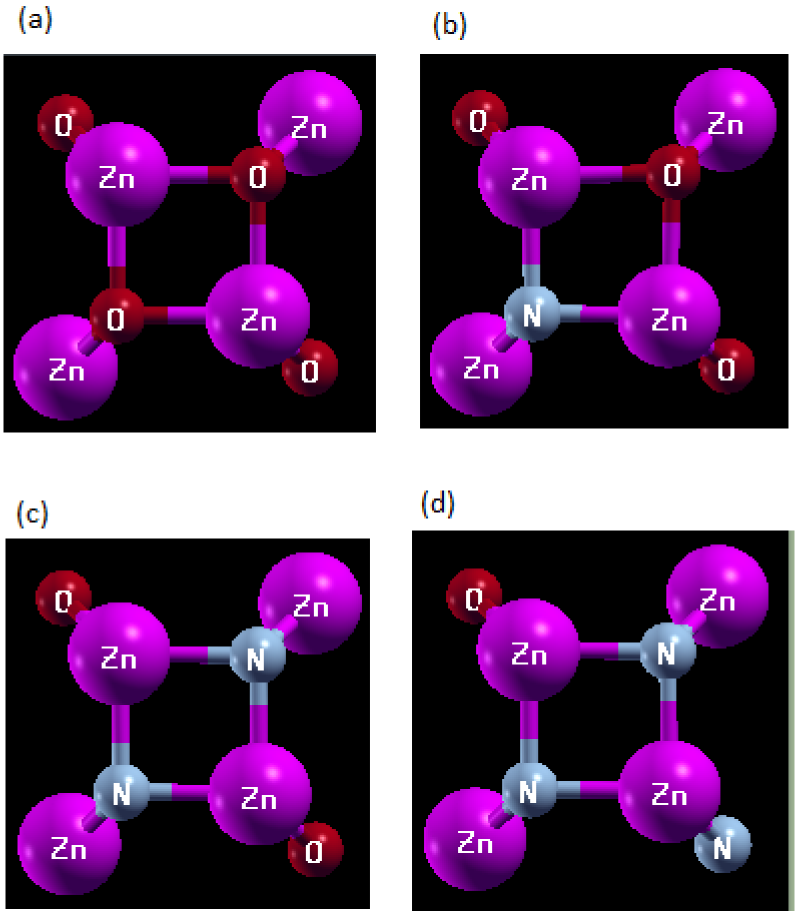


Figure 1: The DFT-GGA Optimized Crystal Structure of: (a) Pure ZnO (b) 12.5 % N doped ZnO (c) 25 % N doped ZnO (d) 37.5% N doped ZnO.

The stability of the doped structures was found by calculating the defect formation energy, E_f, using equation 1 (Zhanghong, 2019).

$$E_f = E_{ZnON} - E_{ZnO} + E_O - E_N \qquad (1)$$

Where, E_{ZnON} is the total energy of the doped super cell, E_{ZnO} is the energy of the undoped supercell, E_O is the energy of the bulk O and E_N is the energy of the impurity atom.

However, to establish whether there are changes on the geometric structure of the material after doping, some important structural parameters for both the pure and doped ZnO were calculated and shown in table 1. The bond lengths of the systems were estimated using equation 2 (Benaicha, 2021).

$$L = \left(\frac{a^2}{3c^2} + \frac{1}{4}\right) c \qquad (2)$$

Where, a and c are lattice parameters.

Table 1: The lattice parameters, volumes, formation energies and bond lengths of the pure and nitrogen doped ZnO.

Model	$\boldsymbol{a}$(Å)	$\boldsymbol{c}$(Å)	$\boldsymbol{c/a}$	$\boldsymbol{V}$ (Å^3)	$\boldsymbol{E_f}$ $(\boldsymbol{eV})$	$\boldsymbol{L}$(Å)
Undoped ZnO	5.529	3.258	0.589	99.57407		3.107
$ZnO_{1-0.125}N_{0.125}$	5.554	3.220	0.580	99.31044	-2.631	3.998
$ZnO_{1-0.25}N_{0.25}$	5.555	3.207	0.577	98.83854	-1.723	4.009
$ZnO_{1-0.375}N_{0.25}$	5.562	3.193	0.574	98.54182	-0.815	4.028

The results (from table 1) showed that the stability of the material decreases as the concentration of doping increases. This is deduced from the increase in the formation energy as the doping concentration increases-the most stable structure is the one having the lower formation energy. It can also be seen from the table that the change in the lattice constants is negligible. This may be due to the closeness in ionic radius of nitrogen (N^{3-} = 0.0146nm) to that of oxygen (O^{2-} = 0.0140nm), and this is also the reason why the pure ZnO material has not undergone any significant deformation during the doping processes. On the other hand, the result showed that the bond length increases with increasing nitrogen concentration.

3.2. Electronic properties

We explain the electronic properties of the pure and nitrogen doped ZnO systems based on electronic band structure, total density of states (TDOS) and partial density of states (PDOS).

3.2.1. Band structure

The result for the band structure reveals that the pure ZnO has a direct band gap of 0.79 eV which occurs between the minima of the conduction band (CB) and the maxima of the valence band (VB) at the high symmetry point (Γ). The maxima of the VB are at 6.4388 eV (the Fermi energy) as shown in figure 2(a).

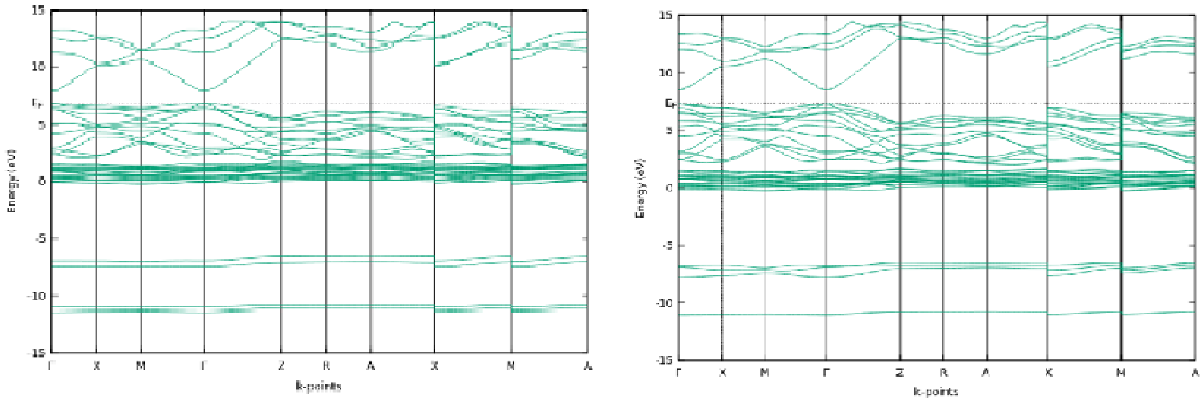
However, though our calculated value for the band gap is less than the experimental value of 3.37 eV, but it is within the range of other theoretical works reported using DFT-GGA such as 0.822 eV (Soleimani, 2017) and 0.671 eV (Bustanafruz, 2016). And generally the lower value of the band gap is due to the well-known underestimation behavior of the DFT-GGA and DFT-LDA to the bandgaps of materials.

Figure 2(b) shows that doping ZnO with N, for $ZnO_{1-x}N_x$ (x=12.5%) has the effect of reducing the band gap of the pure ZnO from 0.79 eV to 0.621 eV thereby decreasing the band gap by about (21%). This shrinkage of the band gap is due to the existence of Zn-N bond having smaller ionicity than Zn-O bond (Kumar, 2007). On the other hand, further increase in the concentration of the dopant, i.e. $ZnO_{1-x}N_x$ (x=25%), made the band gap to expand to 1.03 eV as shown in figure 2(c), and figure 2(d) showed how 37.5% nitrogen doped ZnO increased the band gap to 1.73 eV. .

Experimentally, it has shown that, addition of nitrogen into zinc oxide decreases its band gap (Sutanto et al). The shrinkage in the band gap may be connected to the existence of Zn-N bond with smaller iconicity than Zn-O bond and the widening in band gap seems to be resulted due to the Burstein-Moss (BM) effect if the ZnO thin film has heavy carrier concentration (Kumar, 2007).

c. 25% N-doped ZnO

d. 37.5% N-doped ZnO



a. Undoped ZnO

b. 12.5% N-doped ZnO

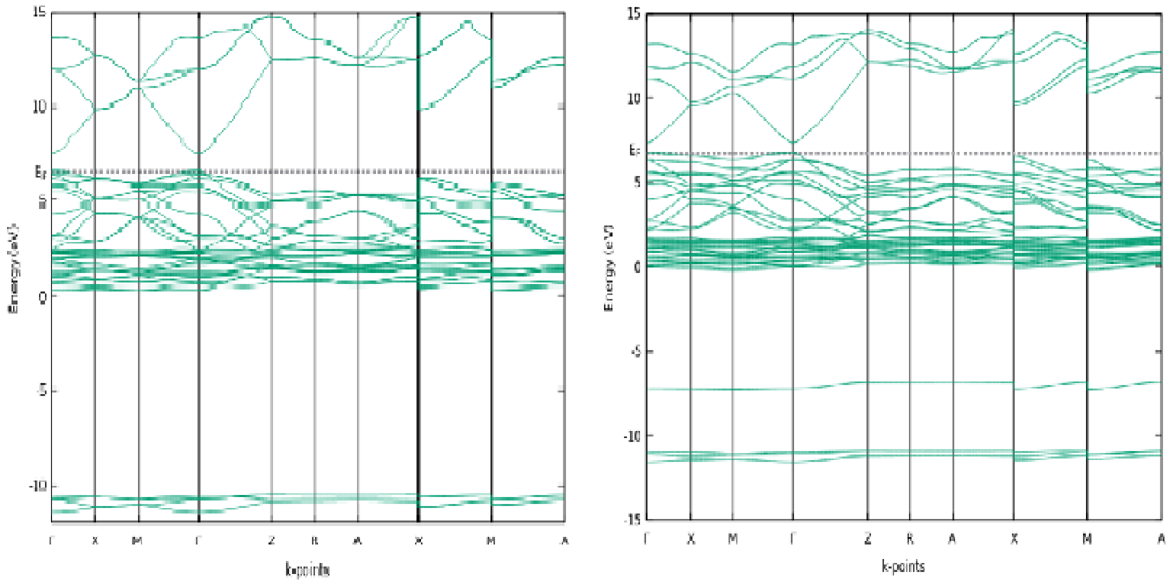


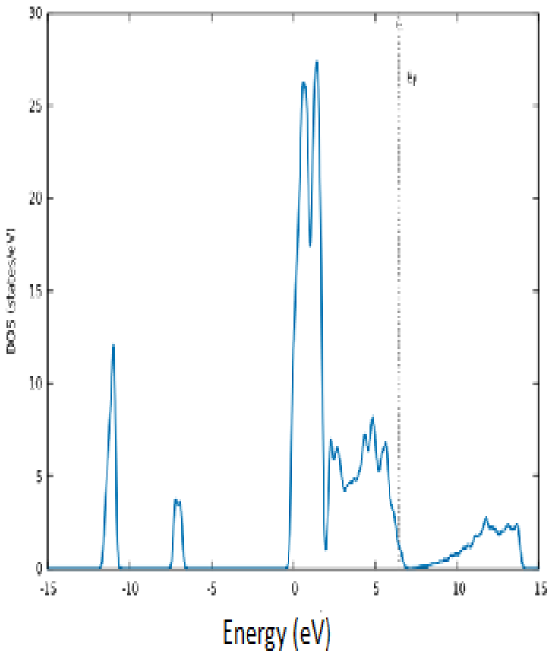
Figure 2. Band structure diagram for ZnO under different nitrogen concentration

3.2.2. Density of state (DOS)

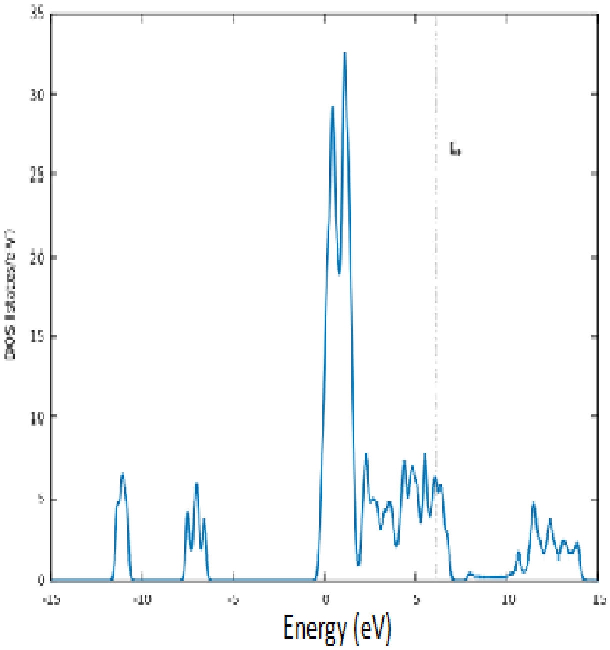
Figure 3(a) showed the density of state of the pure ZnO material. The figure tells us the possible number of states available for occupation at different energy levels of the system. However, figure 3(b) reveals that the valence band (VB) of the pure ZnO consists mostly of the Zn-4s and O-2s states together with Zn-3d states which is dominant between -0.35 eV and 6.74 eV. On the other hand, the conduction band (CB) contains the contribution from Zn-4s states which dominates the region between 9.16 eV to 14.18 eV with O-2p states giving the least contribution. The orbitals Zn-4s and O-2p appear in the same state with the Zn-3d which gives the maximum contribution below the Fermi level.

From figure 3(e), it is deduced that for the nitrogen doped zinc oxide systems , the N-2p states gives its most contribution in the valence band where it shares the same state with Zn-3d, Zn-4s and O-2p orbitals , but contributes least in the conduction band.

(a) Total DOS for undoped ZnO



(b) Total DOS for 12.5% N-doped ZnO



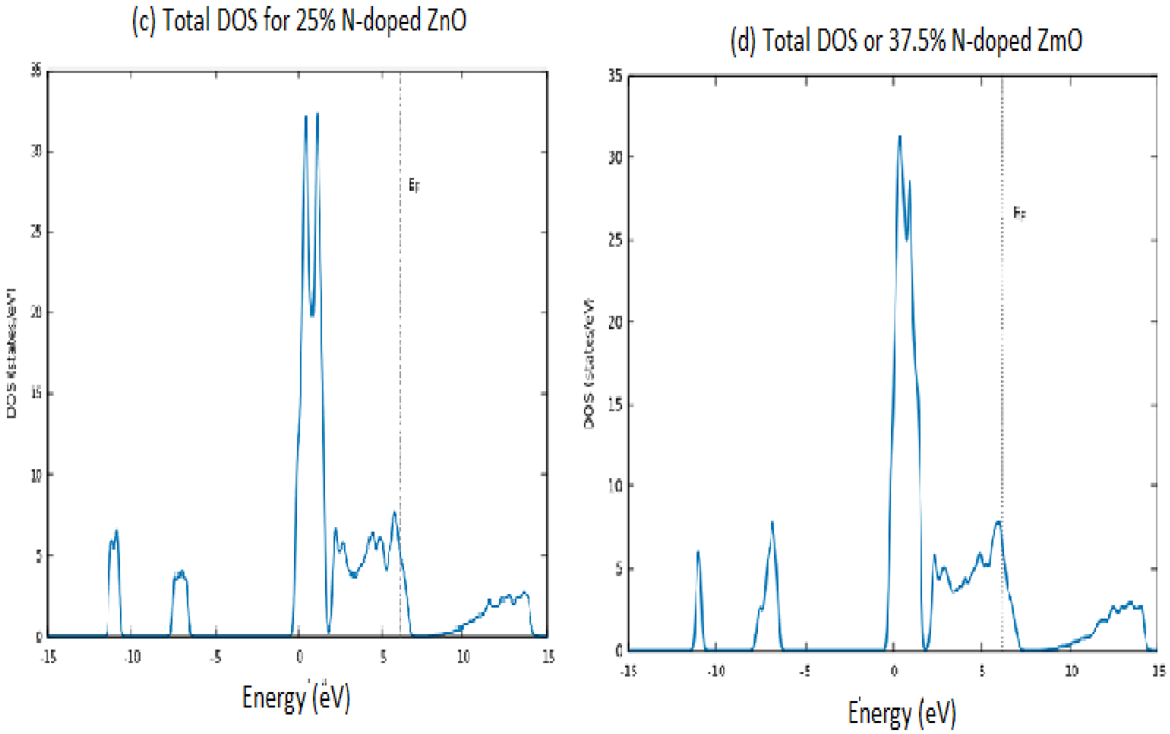


Figure 3. The Calculated Total Density of State under different nitrogen doping concentration

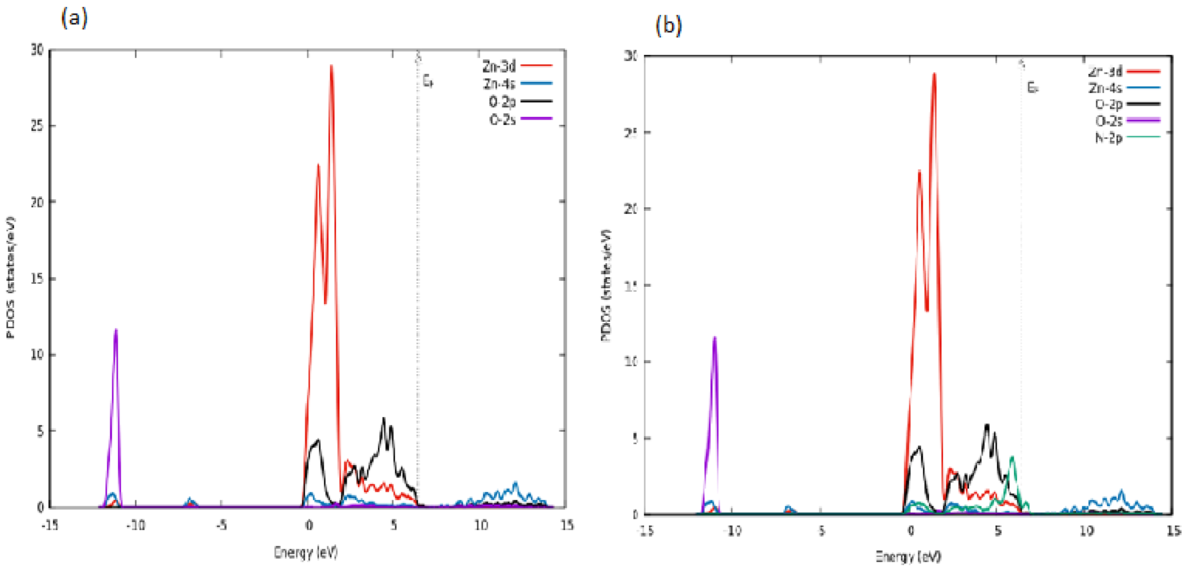


Figure 4. The calculated Partial Density of State for (a) undoped ZnO (b) N-doped ZnO

4. Conclusion

This work reports the effect of nitrogen doping on the geometric structure and electronic properties of ZnO using density functional theory approach. Our result shows that the lattice parameters obtained are in reasonable agreement with both the experimental and theoretical findings. However, the nitrogen doping did not cause any noticeable lattice distortion of the material and the most stable structure is the one with the lower doping concentration. The electronic band structure calculations confirmed a direct band gap in ZnO and also revealed a decrease in the band gap of the material that occurred when the concentration of the doping is around 12.5% but widened when the dopant concentration is 25% which is possibly due to the Burstein-Moss effect.

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