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FIRST PRINCIPLES STUDY OF STRUCTURAL AND ELECTRONIC PROPERTIES OF Ti DOPED ZnO

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The structural and electronic properties of pure and Ti doped (6.25%) Zinc Blend-Zinc Oxide (ZB-ZnO) has been investigated by WIEN2k code based on Density Functional Theory (DFT). The band gap energy will be discussed by studying exchange correlation energy as a functional of density and external potential with the help of simplest approximations. In order to produce accurate band gap we have used Engel-Vosko Generalized Gradient Approximation (EV-GGA) for pure ZnO. By using the EV-GGA model the value of pure ZnO is 1.2 eV direct band gap. Previous value of band gap for pure Zinc oxide is 0.8 eV with GGA model. It was found that Ti doped ZnO band gap is decreased at doping concentration 6.25%. The Fermi level shifts towards the conduction band and material tend to shift towards metallic nature due to strong hybridization of d states of Ti and p states of O.

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1. Introduction

Zinc oxide (ZnO) is a II–VI compound semiconductor with a wide direct band gap of 3.3eV at room temperature and a free-exciton binding energy of 60meV. ZnO has received considerable attention due to its applications such as: gas sensor devices, transparent electrodes, piezoelectric devices and solar cells [1-6].

Mostly semiconductors have tetrahedral coordinate sp^3 covalent bonding nature, but these materials have remarkable iconicity that gives II-VI binary compound semiconductors a unique ionic character such that its ionic character lies at the boundary between covalent and ionic semiconductors [7-8]. The structural geometries shared by ZnO are: Wurtzite (B4), Zinc- Blend (B3), Rock-Salt (B1). Zinc- Blend (B3) structure is the focus of present study as it is stable at 4Gpa and possess a simple cubic structure.

ZnO is unstable material at room temperature; the instability of ZnO is due to position of Oxygen atoms in Zinc Oxide compound. Transition metals are suitable dopant in ZnO to increase the structural, electrical, optical and magnetic properties of the materials. The transition metals are of high melting points, boiling points, densities and have certain characteristics feature including the ability to form complexes and coloured ions. As the transition metals (TM) have incomplete or partially filled d and f orbital, due to these characteristics TM itself exhibit paramagnetic as well as ferromagnetic materials [9]. Transition metals (TM) can easily be mixed with TM's or other elements to form alloys for different uses based on varied hardness strength, malleability, and anticorrosion properties. Recently, ZnO is alloyed with various transition metal ions (TM) to explore its utility in the field of spintronics [10-11].

Now a day, a lot of research has been done on theoretical and experimental basis to study fundamental properties of existing materials and new materials research. Theoretical studies are

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based on analytical models or computer simulations. The density functional theory (DFT) is one of the most accurate and effective microscopic theories in computational materials science, which efficiently describes the ground-state physical properties of electronic systems using LDA-PW91 or GGA-PBE as the exchange-correlation energy functional [8-10]. Calculations in these local (semi) approximations are sufficiently accurate and are helpful for interpretation of experimental data regarding ground-state properties. However, DFT calculations with GGA-PBE do not properly reproduce the excited-state properties, which results in underestimation of the band gap and over estimation of electron delocalization, particularly for systems with localized d and f electrons. In this approximation, the orbital-independent potential is taken in to account to calculate the Kohn–Sham energy gap, which is not comparable to the true gap, which is the ionization potential I minus the electron affinity. Another form of exchange correlation (XC) potential suggested by Engel and Vosko (GGA-EV) yields better values for the band gap calculation [11–17].

In this research work, we will investigate the pure and Ti doped (6.25%) ZnO (ZB-B3) structure to study the structural properties (lattice constant) and electronic properties (density of states and band gap) using Engel and Vosko Generalized Gradient Approximation (GGA-EV) WIEN2K code based on Density Functional Theory.

2. Computational methods

The First-principles calculations were performed using a plane-wave pseudopotential method as implemented in the WIEN2K code. For the exchange correlation potential, the EV-GGA was employed, and the GGA functional given by [18] was used. The convergence tests of the total energy with respect to the plane wave energy cut off and k-point sampling have been carefully examined. The final set of energies was computed with an energy cut off of 1000 eV, and integration using 5 5 3 k-points sampling over the irreducible Brillouin zone, generated by the [19].In order to obtain the special band structure, seven high symmetrical points in the Brillouin zone were chosen as the integral path. Forces on atoms were calculated, and atoms were allowed to relax using a conjugate gradient algorithm until their residual forces had converged to less than 0.005eV/A˚. The calculations were found to be converged to better than 0.002eV/atom with these parameters. The electronic ground state was determined through conjugate gradient minimization of the total energy with respect to the plane wave coefficients. All the Ti-doped ZnO calculations were default spin polarized.

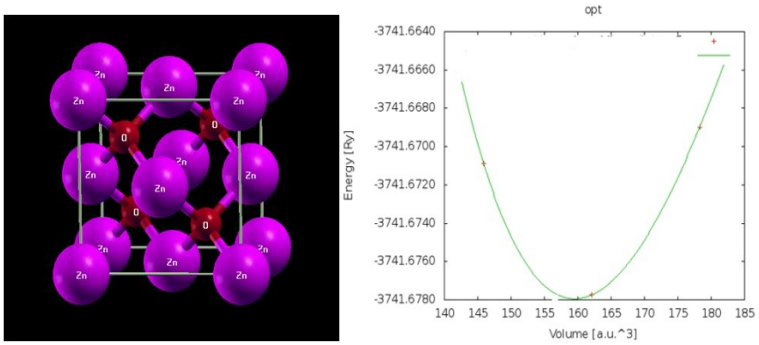
Based on the optimized structure parameters for the perfect crystal, ZnO supercell was constructed for defect calculations. ZnO has a blend structure in which anions and cations, respectively formed simple cubic structure. To simulate the $Zn_{1-x}Ti_xO$, the supercell approach was employed. We thus extended the original ZnO unit cell of four atoms to a 2 2 2 supercell of 32 atoms, i.e., the unit cell size was doubled in all the three crystallographic axes. The supercell contains 16 molecules of ZnO. Two doping levels were considered: for x¼ 0:125, two Zn atoms were substituted by Ti, while for x¼ 0:0625 only one Zn is substituted. Total energies were calculated for x¼ 0:125, and the density of states (DOS) and band structure calculations were achieved for x¼ 0:0625.

3. Results and discussion

3.1 Structural properties

3.1.1 Pure ZnO

The structural properties of Zinc Blende Zinc Oxide in B3 (cubic) phase are calculated by using WIEN2k code. Fig.1 (a) shows supercell of 1×1×1 containing 8 atoms, each oxygen atoms is attached with four zinc atoms. The calculated values of Lattice constants i.e. a=b=c= 4.56 A^0 are in good in agreement with experimental calculated values i.e. 4.58 A^0[20]. Fig.1 (b) the R_{MT} value 5% was used, the value of Zn at this percentage was 1.86 a.u and for oxygen 1.64 a.u.

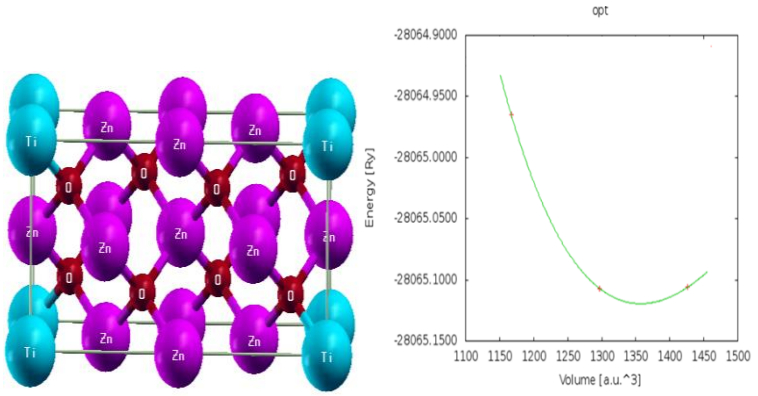


(a) (b)

Fig.1.(a) 3D Structure b) Optimization of pure ZnO with EV-GGA.

3.1.2 Ti Doped ZnO

The selected concentrations of the dopants Ti were 6.25% and its effect on structural parameters i.e., lattice constant and cell volume of ZB-ZnO was observed by using EV-GGA. Fig.2 (a) In this structure the one Ti atom is replaced at first corner from the Zn site. For 6.25% concentration, firstly, the unit cell is composed of 32 atoms which consist of equally number (16) of Zn and O atoms, then selected the single program for formation of super cell of 1×2×2. Initialized cycle is processed step by step, Resultant material obtained a chalcopyrite type structure (ZnTiO) with space group P-4m2 (No.111) after doping of Ti atoms. The (WC-GGA Cohen 6) potential model and cut off energy (-7 Ry) was selected. After that Brillion zone is formed with help of k points which is 100 k points and 6 points generated k-mesh 5×5×2. The calculated values of lattice constant and cell volume for Ti doped ZB-ZnO were 4.59 A° and 1350 a.u.^{3}. This increment in lattice constant of Ti doped ZnO compared to pure ZnO results in band gap decrement.



(a) (b)

Fig. 2. (a) 3D Structure b) Optimization of Ti doped ZnO with EV-GGA.

3.2 Electronic properties

3.2.1 Density of states

Fig.3 (a) shows the Density of states of pure ZnO. Valence band is mainly originates from a mixture of Zn-3d with O-2p states. The top of the valance bands are mainly from O-2p states. The Zn-3d states are major at lower energies ZB phase the O-2p states are major at lower energies. The C.B is mainly formed by the Zn-4s states. A high dispersion of d band is because of the strong hybridization of p and d orbital in the V.B that pushes the O-2p states closer to the C.B that results in the band gap narrowing. Fig. 3 (b) shows that density of states (DOS) of Ti dopants lie at Fermi

level with the dopant concentration of 6.25% because DOS showed strong hybridization of p-state of O with d-states of Ti. Consequently, the host material shifts its behavior towards metallic alloy.

3.2.2 Band gap

Fig.4 (a) shows that V.B of pure ZnO is mainly formed from O-2p and Zn-3d orbital and the conduction band is originated mostly form Zn-4s orbital. A strong hybridization between p and d orbital occurs that pushes the 2p orbital of O very close to 4s orbital of Zn, that results in the narrowing of the band gap. The band structure of pure ZnO shows the direct band gap in ZB-ZnO (B3) phase. The calculated result of band gap is 1.2 eV using EV-GGA. The difference between the minima of conduction band and maxima of valance band lies at same line $\Gamma - \Gamma$.

Fig.4 (b) the band structures of Ti doped (x = 6.25%) ZnO shows metallic behaviour. The band structure of alloy exhibits overlapping of the conduction and valence bands to each other. Fermi level is shifted toward the conduction band which may be considered as a strong reason of its conversion into the ferromagnetic material. The magnetic nature of Ti doped ZnO was also studied [4].

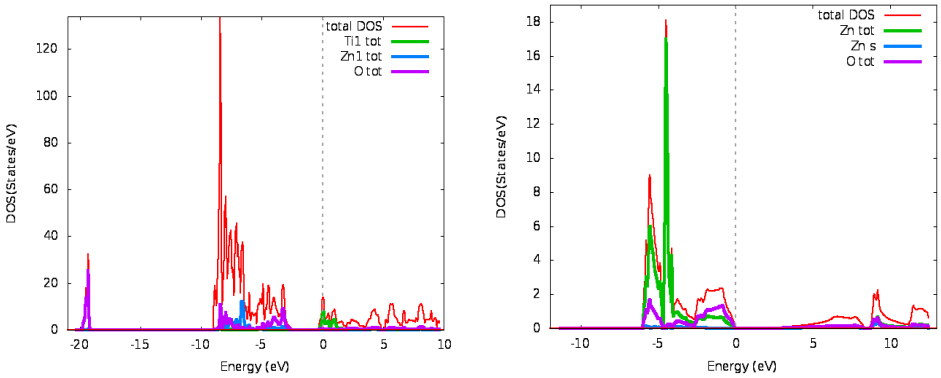


Fig. 3.Density of States of a) pure and b) Ti-doped ZnO.

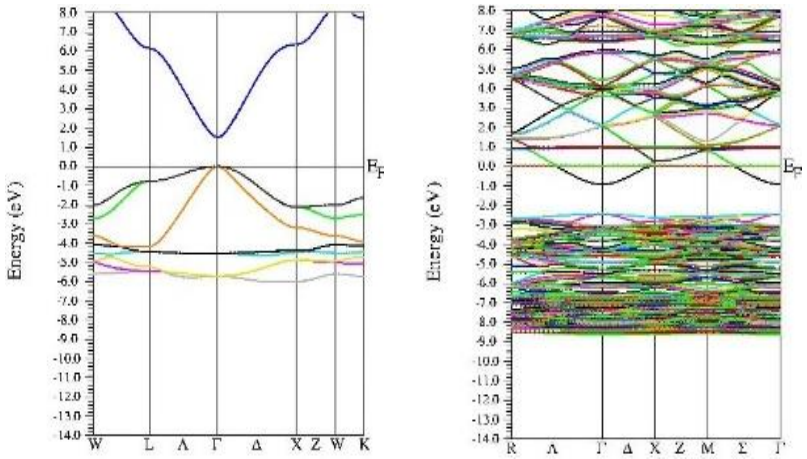


Fig. 4. Band gap of a) pure and b) Ti doped ZnO.

4. Conclusions

The structural and electronic properties of pure and Ti doped (6.25%) Zinc Blend-Zinc Oxide (ZB-ZnO) was investigated using WIEN2k code based on Density Functional Theory

(DFT). It was found from structural analysis that values of lattice constant of pure ZB-ZnO and Ti doped was 4.56 A^0, 4.59 A° respectively. The increment in lattice constant of Ti doped ZnO shows band gap decrement. It was found from electronic properties that density of states of Ti dopants lie at Fermi level which showed strong hybridization of p-state of O with d-states of Ti atoms. The band structures of Ti doped (6.25%) shows metallic behaviour. Fermi level is shifted toward the conduction band which may be considered as a strong reason of its conversion into the ferromagnetic material.

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