First principle study of structural, electronic, optical and electrical properties of Ga doped ZnO with GGA and mBJ approximations

M Khuili¹, N Fazouan¹, H Abou El Makarim², G El Hallani¹ and E H Atmani³
¹Laboratory of Materials Physics, Faculty of Sciences and Technologies, B.P 523, 23000 Beni Mellal, Morocco.
²Laboratory LS3ME, Team Theoretical Chemistry and Molecular Modeling, University of Mohammed V, Faculty of Sciences, Department of Chemistry, BP1014 Rabat Morocco.
³Laboratory of condensed matters and renewables energies, Faculty of Sciences and Technologies, B.P 146, 20650 Mohammedia, Morocco

E-mail: fazouan@yahoo.fr

Abstract. Physical properties of Gallium doped ZnO in wurtzite phase has been studied. We have used the Generalized Gradient Approximation (GGA) to determine the structural parameters of each concentration of Ga. The modified Becke–Johnson potential TB-mBJ has been used to calculate the partial and total density of states. The dielectric function, refractive index, optical reflectivity, absorption coefficient and transmittance spectra were predicted using the same potential. The calculated energies of bands structure has been used with the Boltzmann transport equation to calculate the electrical conductivity of Ga doped ZnO. We have observed that the donor concentration, optical band gap and electrical conductivity can be widely tunable with the doping levels of Ga. The results of pure and doped ZnO were in agreement with experimental and other theoretical studies. The obtained results confirm that Ga doped ZnO is a transparent conductor dedicated for applications in photovoltaic devices.

1. Introduction
Transparent conductive oxides (TCO) thin films are materials which have good optical transparency in the visible range and high electrical conductivity. These two characteristics of TCOs depend on the nature, number and atomic arrangement in the crystalline structure, the morphology of the layer and the presence of intrinsic (oxygen vacancies and interstitials of the metal) or extrinsic (dopants) defects. Zinc oxide is one of the TCO, frequently used in several areas such as solar energy and optoelectronics [1],due to its thermal stability [2]. Its wide band gap 3.37eV which allows it to be transparent to visible and infrared radiation, and its large exciton binding energy (60meV) [ 3]. To enhance its electrical conductivity, Zinc Oxide is usually doped with group III elements such as Ga, B, Al and In as effective donors [4]. Gallium doped zinc oxide has comparable structural and optical properties as pure ZnO seen its ionic and covalent radiuses, which are similar to those of Zn, and is a desirable material for many applications. Moreover, there are studies, which classify it better
conduction stability than Al doped ZnO for the reason that Ga has low reactivity and better resistivity to oxidation than Al [5].

Many theoretical studies have used ab-initio methods, to determine structural, electronic, optical and electrical properties of pure and doped ZnO, and also the percentage of doping to be used to get a material with clearly defined properties. However, density functional theory (DFT) underestimates the band gap of many transition metal oxides as ZnO. For example, the band gap calculated of pure ZnO is about 0.77 eV by the Generalized Gradient Approximation (GGA) [6] which is smaller than experimental results 3.4eV [7]. To get a correct band gap, many theoretical studies was introduced such as GGA+U [8], the Heyd–Scuseria–Ernzerh (HSE) of screened hybrid density functional [9] and GW implementations [10]. The last two methods lead to very expensive time calculations. Recently, Tran and Blaha introduce exchange–correlation potential TB-mBJ [11] which allows to have band gap values similar to those found by the hybrid functional in reasonable time calculation.

In this study, we report the structural, electronic, optical and electrical properties of Ga doped ZnO with different Ga concentrations. To calculate these properties, we employ density functional theory (DFT) employing the Full Potential Linearized Augmented Plane Wave (FL-LAPW) and using TB-mBJ in order to have a good estimate of the optical gap approaching the experimental value.

2. Computational methods

We have employed FP-LAPW approach as implemented in the WIEN2k code [12]. A revised Perdew-Burke-Ernzerhof exchange-correlation functional PBEsol[13] is used to study the structural properties of our material. The electronic, optical and electrical properties are determined using TB-mBJ approximation. The values of the smallest muffin tin radius of atoms RMT were chosen as 1.93 a.u. for zinc, 1.66 a.u. for oxygen and 1.87 a.u. for gallium, and an energy cutoff $K_{max} \times R_{MT} = 7.5$ was used. The complex dielectric in this code is expressed by the well-known relation,

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

the optical constants, absorption coefficient $\alpha(\omega)$, reflectivity $R(\omega)$, and transmittance $T(\omega)$ can be derived from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$:

The imaginary part of the $\varepsilon_2(\omega)$ in the long wavelength limit has been obtained directly from the electronic structure calculation [14].

$$\varepsilon_2(\omega) = (4\pi e^2 / \omega^2 m^2) \sum_{i,j} \int |i | M_{ci} |j^2 f_i (1 - f_i) \ast \delta(\varepsilon_f - \varepsilon_i - \omega) d^3 k$$

$M_{ci}(k)$ The transition moments elements, $i$ the initial states and $j$ the final states, $f_i$ is the Fermi distribution.

The real part of the dielectric function follows from the Kramers-Kronig relation [15]

$$\varepsilon_1(\omega) = Re(\varepsilon(\omega)) = 1 + (2/\pi) P \int_0^\infty \omega' \varepsilon_2(\omega') / (\omega'^2 - \omega^2) d\omega'$$

Where P implies the principal value of the integral

The absorption coefficient $\alpha(\omega)$and the reflectivity $R(\omega)$ follows from Fresnals formula[16]:

$$\alpha(\omega) = \omega \sqrt{\varepsilon_1(\omega) + \varepsilon_2(\omega) - \varepsilon_1(\omega)}^{1/2}$$

$$R(\omega) = \left[ \frac{(\varepsilon(\omega) - 1)^{1/2}}{(\varepsilon(\omega) + 1)^{1/2}} \right]^2$$

To obtain the electrical conductivity we have used the BoltzTrap package [17] based on semi-classic Boltzmann theory which use the calculated band structure data obtained from wien2k.
3. Results and discussion:

3.1. Structural parameters

Zinc oxide often crystallizes in a hexagonal wurtzite structure belonging to space group P63mc [18]. This structure is known by three parameters: the parameter of the cell a, the ratio c/a and the internal parameter u, which must be optimized. The ground state lattice constants of Ga doped ZnO are obtained by using 2D-optimize package available in the Wien2k code [19]. It helps to have a good volume and c/a simultaneously for solid better than those obtained by the 1D based on the minimization of energy by volume. First, we get value of c/a, therefore the energy for each volume, then for those volumes and energies the equation of state (EOS) will be obtained, and finally the optimum value of c/a is calculated from optimal volume. From these results of calculated parameters a and c, we found that they increase with increasing concentration of the incorporation of Ga into ZnO. In the Figure 1 we plotted the calculated lattice constants a and c versus doping concentration of Gallium. Results show that the a and c parameters increase slightly with increasing Ga concentration. This change in lattice constant caused by Ga doping ZnO is due to difference between effective ionic radii between Ga$^{3+}$ (0.57 Å) and Zn$^{2+}$ (0.74 Å) and by Mulliken charge of Zn, Ga and O leading to a weak attractive coulomb interaction which extends the bond lengths of Zn–O and Ga–O when the Ga concentration increases as reported by H.C Wu et al. [20].

![Figure 1](image)

**Figure 1.** The lattice constants as a function of Ga concentration for (x=0, 3.125%, 6.25% and 12.5%).

3.2. Electronic structure

In this section, Figure 2 shows the band structure of pure ZnO and doped ZnO with 6.25% of Gallium. The band structure is calculated at the theoretical equilibrium configuration wurtzite, using our optimized lattice constants. Zinc oxide displays a direct band gap of about 2.8eV which is in a good agreement with experimental values [21] calculated between the minimum of the conduction band and the maximum of the valence band at $\Gamma$-point. In the case of Ga doped ZnO at 6.25%, the Fermi level shifts upward into the conduction band, the band gap is measured between the valence band maximum and the Fermi level in the conduction band [20,22]. The same we have calculated the band gap for the others concentrations of Ga, which are presented in the table 1, and compared with other theoretical and experimental values. We found that increasing the Ga concentration shift up the band gap value, which can be explained by producing a degenerate n-type semiconductor related to a pronounced Burstein–Mott-effect [23, 24].
### Table 1: Calculated band gap for various concentration of Ga

| Concentration of Ga | Calculated band gap (eV) | Theoretical band gap (eV) [20] |
|---------------------|--------------------------|-------------------------------|
| 0%                  | 2.79                     | 3.37                          |
| 3.125%              | 3.34                     | -                             |
| 6.25%               | 3.95                     | 4.37                          |
| 12.5%               | 4.32                     | 5.5                           |

![Figure 2](image-url)  
Figure 2. Band structure of (a) pure and (b) Ga doped ZnO in a 2x2x2 supercell

The calculated density of states (DOS) and partial density of states (PDOS) are shown for pure and Ga doped ZnO in Figure 3. The valence band essentially consists of the 2p and 2s states of O and 3d states of Zn. In the uppermost valence band, O 2p states are found between -4 and 0 eV. While the O 2s states appear in the range from -18 to -16 eV. The position of peak of Zn 3d plays an important role in the electronic structure of ZnO system. From PDOS of Zn, we can see that the upper valence band -6eV to 0eV is dominated by Zn 3d with high intensity. In addition, the lowest conduction band is dominated by Zn 4s states, and experimental results also indicate that it is primarily derived from O 2p and Zn 4s states. The calculated band gap with GGA is found in our case around 0.8eV due to the hybridization between the Zn 3d and O 2p levels. The introducing of the potential TB-mBJ can correct the energy level of Zn 3d states to -6.2eV and the gap value improve, to 2.8eV. The hybrid functional, such as PBE0 and HSE, can shift the Zn 3d states to -5.8, -5.9 and -6.4, and the gap is 3.24–3.26, that is very close to the experimental value of 3.4eV, but it is computationally expansive [25].
The total and partials densities of states (TDOS, PDOS) of pure and Ga doped ZnO in 2x2x2 supercell (x = 6.25%) are plotted in the same figure 3. Here we find that the Ga-3s orbital contributes to the occupied states around Fermi level. These donor states around the Fermi level could be considered as the origin of the conductivity increasing in Ga doped ZnO sample.

### 3.3. Optical properties

The optical band gap (E_g) of pure ZnO and Ga doped ZnO was estimated by Tauc relation [26]:

$$\alpha h\nu = A (h\nu - E_g)^n$$  \hspace{1cm} (6)

In this equation, $\alpha$ is absorption coefficient, $h\nu$ is photon energy, and $A$ is the proportionality constant for a direct interband transition. The power $n$ is equal to the $\frac{1}{2}$ since ZnO is a direct band gap material. We have plotted the $(\alpha h\nu)^2$ vs $h\nu$ for various concentrations, and fitted for the straight region. The extrapolation of this straight line to $h\nu$ axis gives the value of the band gap. Figure 4 shows that the value of band gap $E_g$ increases with increasing Ga doping concentration. This is attributed to Moss-Burstein effect, caused by an increase in free electron concentration due to Ga doping.

![Figure 4](image.png)

**Figure 4.** Plot of $(\alpha h\nu)^2$ versus $(h\nu)$
To determine the other optical properties of the Ga doped ZnO, it is necessary to calculate the imaginary part, and the real one of the dielectric function $\varepsilon_2$ and $\varepsilon_1$ respectively. From which the optical constants, such as refractive index $n(\omega)$, absorption coefficient $\alpha(\omega)$, reflectivity $R(\omega)$, and energy-loss spectrum $L(\omega)$ are derived [27].

Reflectivity as a function of wavelength in the range of 250–900 nm at various Ga concentrations is displayed in the Figure 5a. As the Ga concentration increases from 0 to 12.5 at. %, the reflectivity decreases and rest less than 7%.

Figures 5b and 5c show the absorption coefficient and optical transmittance spectra respectively at various Ga concentrations. The average transparency in the visible range was around ~80-90%. It appears that doping ZnO with Ga results in an improvement of transmission in the wider range of the solar spectrum. Except at higher doping concentrations (12.5%) showing a reduction in the transmittance, which is explained experimentally by the increased scattering of photons by crystal defects created by doping [28]. The absorption edge is blue shifted with increasing Ga doping concentration, which means broadening of the optical band gap, related to Burstein-Moss effect.

![Graphs showing reflectivity, absorption, and transmittance](image)

**Figure 5.** The variation of (a) reflectivity, (b) absorption coefficient, and (c) transmittance for doped ZnO with various Ga concentrations.

### 3.4. Electrical properties

Based on the calculated electronic band structures and the semi-classical Boltzmann equations with the relaxation time approximation were used to evaluate the electric transport coefficients for pure and Ga doped ZnO for various concentrations.
Using the electronic structure it is possible to calculate $\sigma/\tau$ as a function of $n$ and $T$, where $\tau$ is the relaxation time in second, $T$ the temperature in Kelvin, $n$ the carriers concentration in cm$^{-3}$ and $\sigma$ the conductivity in $(\Omega \text{cm})^{-1}$. But it is not possible to calculate $\sigma$ itself without knowledge of the scattering rate $\tau^{-1}$. In order to proceed, we use relationship written by Ong et al.[29]:

$$\tau = 2.53 \times 10^{-5} T^{-1} n^{-1/3}$$  \hspace{1cm} (7)

then we calculate $\sigma$ as $\sigma/\tau \times \tau$ knowing that:

$$\tau = 2.53 \times 10^{-5} T^{-1} n^{-1/3}$$  \hspace{1cm} (8)

Here in the above equations, $f_{\mu}$ is the Fermi distribution function, $\mu$= chemical potential (temperature dependent) and $\Omega$ the volume. The indices $\alpha$ and $\beta$ denote the components of tensor conductivity.

Figure 6 shows electrical conductivity as function of concentration of Ga. From this Figure, we can see at low concentration $\leq 6.25\%$ of Ga the electrical conductivity increases with increasing concentration of Ga, explained by the replacing Zn$^{2+}$ by Ga$^{3+}$ atom which can release one electron to the ZnO material, and increases the mobility and the carrier concentration in the low concentration range. However, the electrical conductivity drastically decreased at the high doping concentration over 6.25% due to the saturation for high concentration of Ga. The difference of ionic radii of Zn$^{2+}$(0.74 Å) and Ga$^{3+}$(0.62 Å), there should be a limit of solid solution of Ga into ZnO crystal and so does the increase of carrier concentration.

**Figure 6.** The electrical conductivity of pure and Ga doped for various Ga concentrations

4. **Conclusion**

In this paper, we have studied the effect of incorporation of Gallium in the Wurtzite Zinc oxide using First Principles and semi-classic Boltzmann theory. We calculate the structural, electronic, optical and electrical properties of Ga doped ZnO at various concentrations of Ga, compared to undoped ZnO. For low concentration of Ga the reflectivity and absorption are reduced, the transmittance and optical band gap is enhanced. Also, the electrical conductivity is increased due to increasing of the donor concentration, but at high concentration of Ga the electrical properties is decreased. The structural parameters and the band gap found are in a good agreement with theoretical and experimental results. These results make this doped material with low concentration of Ga desirable in applications of photovoltaic field.
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