

First-principles calculations of band structures and optical properties of hexagonal ZnO by using meta-GGA in the framework of density functional theory

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Using meta generalized gradient approximations (meta-GGA) to describe the exchange–correlation functional, we performed first-principles calculations on the band structures, density of states, dielectric function, refractive index function, extinction coefficient function and absorption coefficient function for hexagonal ZnO within the framework of density functional theory (DFT). It is found that the calculated band gap of ZnO is in excellent agreement with the experimental values. However, there are significant underestimations in the complex dielectric constant, refractive index, extinction coefficient and absorption coefficient. Although they still fall short of providing a complete and reliable description of the optical properties, our results have demonstrated that the optical properties derived from the DFT based first-principles calculations can be used with reasonable reliability to interpret the optical features of hexagonal ZnO.

Keywords: Band structure; Density functional theory; ZnO; Local density approximation; Meta-GGA

1. Introduction

Zinc oxide (ZnO) has aroused intense interest in the scientific community because of its versatile applications in ultraviolet light emitting phosphors, solar cells, photocatalysts, transparent conducting electrodes, etc [1-6]. Of the three types of its well-known crystal structures, hexagonal-type ZnO is the most stable phase under ambient conditions. Consequently both the electronic and optical properties of hexagonal ZnO were the focus of the extensive studies in the past two decades. As research on ZnO continues to grow at a record-setting pace, increasing demands are placed on the accurate calculations of the electronic structures and optical properties of hexagonal ZnO. Among the numerous computing techniques to calculate the electronic and optical properties of semiconductors, it is identified that density functional theory (DFT) based first-principles methods are a powerful approach to investigate the properties of ZnO [7-10]. In the DFT, the approximation for the exchange-correlation energy is of central importance in the accuracy of DFT-based calculations. As documented in the literature, the local density approximation (LDA) and the generalized gradient approximations (GGA) are often adopted in the DFT based first-principles calculation. However, it is well known that LDA and GGA have problems in reproducing the band gaps of semiconductors, and the DFT based first-principles methods exhibited an increasing number of vulnerabilities, one of which is the significant underestimation of the bandgap of ZnO

mainly due to the use of LDA and GGA. One way of calculating the underbinding of the Zn 3d electrons is to include an on-site Coulomb correlation interaction using the so-called LDA+U method [11], which corrects the position of the narrow d band states and influences both the valence band maximum and the conduction band minimum. A second way of overcoming the limitations of LDA and GGA is to use hybrid functionals but their high computational cost restricts them to small systems [12]. The third approach, which recently has been receiving a lot of attention, is meta-GGA, which has been reliably applicable to different elements, binary compounds, transition-metal oxides, sulfides, metals and ferromagnetic insulators [13,14]. In general, the meta GGA performs the best, the GGA functionals usually perform better than the LDA functional.

In this work, we performed DFT based first-principles calculations on the electronic structures and optical properties of hexagonal ZnO by using meta-GGA as the exchange correlation functional. It was found that the calculated band gap of ZnO was in excellent agreement with the experimental values whilst the calculated optical functions (complex dielectric constant, refractive index, extinction coefficient and absorption coefficient) were significantly underestimated in magnitude.

2. Materials and methods

Hexagonal ZnO belongs to space group P6₃mc with lattice constants of $a = b = 0.3249$ nm and $c = 0.5206$ nm. Each primitive cell contains two O atoms and two

Zn atoms, among which a Zn atom is located in the center of the tetrahedron made up of four O atoms and vice versa. All calculations were performed with lattice constants $a = 0.32495$ nm, $c = 0.52069$ nm and space group $P6_3mc$ for hexagonal ZnO. Fig. 1 shows the crystal structure of the $5 \times 5 \times 5$ super cell of pure ZnO in hexagonal phase. Each red ball in Fig. 1 represents an O atom whilst each grey ball represents a Zn atom. We calculated the electronic and optical properties of ZnO by using the DFT based first-principles method. The calculations were performed using the DFT program package as implemented in the Atomistix ToolKit 11.8. To reduce the computation, the valence electron configurations of Zn and O were considered as $Zn-3d^{10}4s^2$ and $O-2s^22p^4$, respectively. The exchange-correlation energy was calculated using the meta-GGA functionals. The mesh cut-off energy was set to be 150 Ryd. A mesh of $11 \times 11 \times 11$ k-points was used to sample the BZ and a broadening of 0.1 eV was applied.

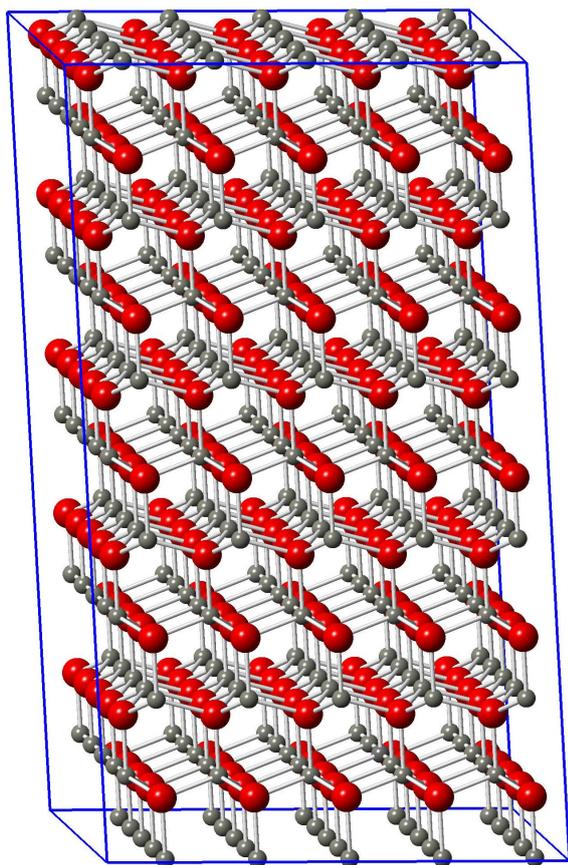


Fig. 1 Crystal structure of the $5 \times 5 \times 5$ super cell of pure ZnO in hexagonal phase. The red and grey balls represent O and Zn atoms, respectively.

Spherical ZnO nanocrystals were synthesized to provide a reference for the evaluation of the band gap and absorption coefficient of ZnO. High quality quartz plates were utilized as the substrates of ZnO films.

Details on the synthesis and morphology of the synthesized ZnO nanocrystals were described elsewhere [15]. After the synthesized ZnO nanocrystals had been dispersed into ethanol to form suspension, a spin coater was employed to develop a thin film on the quartz substrate for the absorption measurement. The thickness of the ZnO film was estimated to be around 100 nm. An ultraviolet-visible spectrometer (Shimadzu UV-2450, Japan) was employed to measure the absorption spectra of the ZnO specimens.

3. Results and discussion

3.1 Band structures and density of states of ZnO

Fig. 2 shows the calculated band structures of pure ZnO in hexagonal phase. The Fermi level is set at zero energy. It can be seen in Fig. 2 that the band gap of ZnO is direct since both the valence band maximum and the conduction band minimum are located at Γ point. The valence band maximum is located at -1.6190 eV below the Fermi level while the conduction band minimum is located at 1.6190 eV above the Fermi level. So the bandgap of hexagonal ZnO is derived to be 3.2380 eV, which is very close to the widely accepted value of ZnO (3.37 eV). When compared to those DFT based calculations with the LDA or GGA approximations [7,9,10], a considerable improvement in the accuracy of the band gap has been achieved by using LDA under PZ parameterization as the exchange-correlation functional.

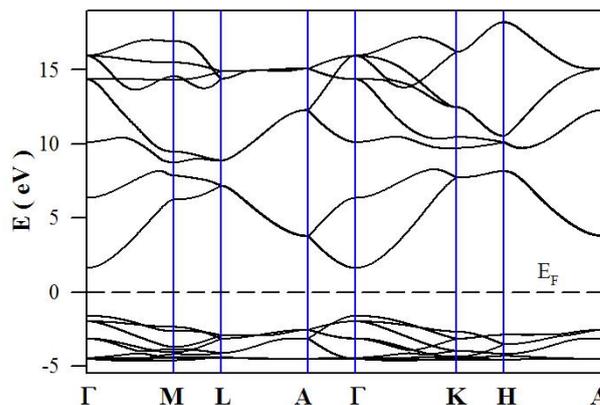


Fig. 2 Band structure of pure ZnO in hexagonal phase.

Both the total density of states (DOS) of ZnO and the partial densities of states of Zn and O atoms are shown in Fig. 3. The dashed vertical line in Fig. 3 represents the Fermi level of ZnO. The two solid vertical lines in Fig. 3 represent the points where the band gap starts and ends. It is clear that the valence band in the range of -1.6190 to -5.0 eV is mainly contributed by O-2p states and Zn-3d states. The lower part of the valence band in the range of -18.6 to -16.0 eV, which is not shown here, is mainly contributed by

O-2s states. The orbital resolved DOS shows considerable hybridization of the Zn-3d state with the O-2p state, hence, the 3d electrons of Zn strongly participate to the chemical bonding of ZnO, and the Zn-3d and O-2p orbitals are strongly admixed in the valence band. In a similar way, we find that the contribution band of ZnO is mainly composed of Zn-4s and O-2p states. These results qualitatively agree well to earlier reports as documented in the literature.

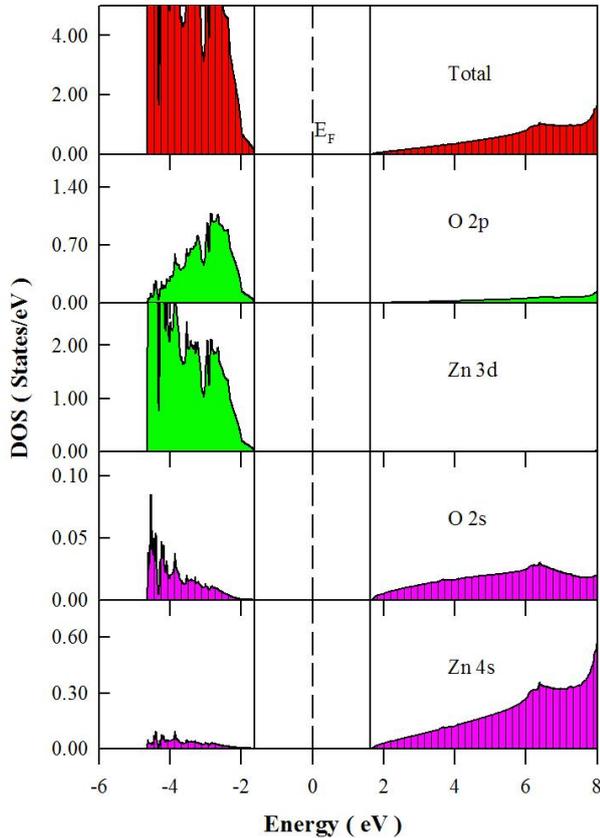


Fig. 3 DOS of pure ZnO in hexagonal phase.

3.2 Dielectric function and optical properties

As we know, the optical properties of the medium can be described by the complex dielectric response function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ in linear response range. The real part $\epsilon_1(\omega)$ and imaginary part $\epsilon_2(\omega)$ can be calculated according to the dispersion relation of Kramers–Kronig. In this way, other optical functions such as the refractive index function, $n(\omega)$, the extinction coefficient function, $k(\omega)$, and the absorption coefficient function, $\alpha(\omega)$, can be obtained. Thus from the dielectric constant a number of other optical properties are easily obtained. The refractive index and the extinction coefficient are related to the complex dielectric constant through the equation 1 as described below

$$n + i\kappa = \sqrt{\epsilon_r} \tag{1}$$

In term of the real (ϵ_1) and imaginary (ϵ_2) parts of the

relative dielectric constant, we can derived

$$n = \sqrt{\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} + \epsilon_1}{2}} \tag{2}$$

$$\kappa = \sqrt{\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} - \epsilon_1}{2}} \tag{3}$$

The optical absorption coefficient is related to the extinction coefficient through

$$\alpha = \frac{2\omega}{c} \kappa = \frac{4\pi}{\lambda} \kappa \tag{4}$$

The above formulae provide a theoretical foundation for the analysis of the band structure and optical properties of the crystals, which reflect the electronic transition between energy levels.

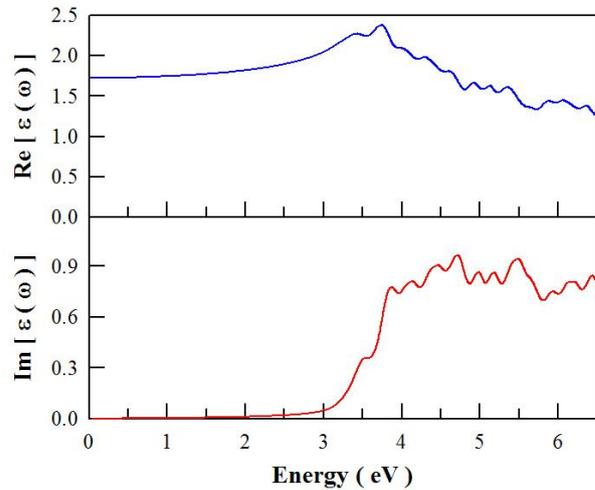


Fig. 4 Dielectric function of hexagonal ZnO.

Fig. 4 shows the complex dielectric function of hexagonal ZnO. As revealed by Fig. 4, no absorption is expected below the band gap energy, and there is a nearly smooth dispersion for the real part of the dielectric function. The real part of the dielectric function increases slowly from 1.72 to 2.27 as the photon energy changes from 0 to 3.4 eV, then it is decreased gradually to 1.24 as the photon energy increases further from 3.4 to 6.5 eV. The imaginary part of the dielectric function of ZnO can be almost neglected when energy is less than 2.5 eV, then it starts its climb at the energy of 2.5 eV until reaching its maximum at around 4 eV. After that the imaginary part of the dielectric constant experiences fluctuations as the energy increases from 4 to 6.5 eV. When compared to the data derived from the spectroscopic ellipsometric measurements, both the real and imaginary parts of the dielectric function are apparently similar in profiles but they are heavily underestimated in magnitude [16–18]. For example, the

real part of the static dielectric constant of bulk ZnO was reported to be about 3.7 whilst its imaginary part was reported to be 2.5 at 3.4 eV [19]. Especially, Agocs *et al.* measured the dielectric function for ZnO layers ($d \approx 50$ nm) with a spectroscopic ellipsometer [20]. It can be found that our calculated dielectric constants are about half of the measured values.

The refractive index is an important parameter for optical materials and applications. Thus, it is important to determine the refractive index and extinction coefficient of the ZnO films. Fig. 5 shows the plots of the refractive index and the extinction coefficient of ZnO against the energy. It is clear that both the refractive index and the extinction coefficient are smaller than the reported data [21–23]. For example, the refractive indices were reported to be 1.89 at 0.31 eV and 2.06 at 2.55 eV [22]. In spite of the value underestimation of the refractive index and extinction coefficient, the resonant energies of the two response functions are located around the band gap of ZnO.

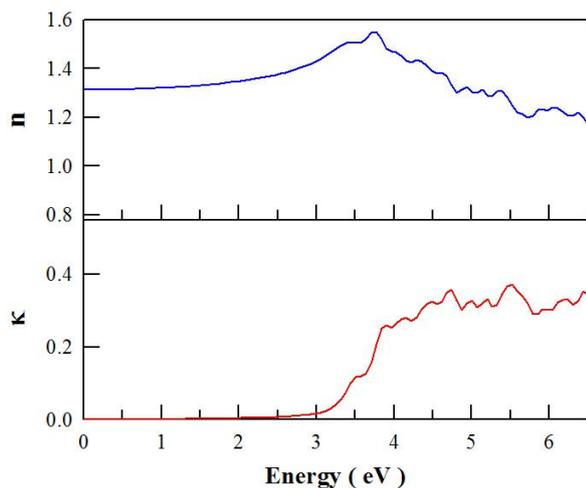


Fig. 5 Refractive index and extinction coefficient of pure ZnO in hexagonal phase.

3.3 Calculated and measured absorption spectra

The ultraviolet–visible absorption spectrum of ZnO nanoparticles can provide reference for the calculated electronic and optical properties of the hexagonal ZnO. Fig. 6 (a) shows the plot of calculated absorption coefficient of hexagonal ZnO bulk as a function of energy. The absorption coefficient of hexagonal ZnO is about negligible when the wavelength is longer than 400 nm, but it exhibits strong absorption in the range of 300–380 nm. As the wavelength is shorter than 400 nm, the calculated absorption coefficient of hexagonal ZnO starts to increase quickly in magnitude. For example, the absorption coefficient reaches to 5×10^4 cm^{-1} at 350 nm, then climbs as high as 1×10^5 cm^{-1} at 325 nm. The calculated absorption coefficient agrees roughly with those measured data in the literature [24].

Fig. 6(b) depicts the plot of the measured absorption coefficient of hexagonal ZnO nanoparticles as a function of photon energy. We have noticed that the thickness of the ZnO thin film was a rough estimation. It is obvious that the absorption spectrum in Fig. 6(b) is quite similar in profile to the calculated plot in Fig. 6(a). A comparison of the data in Fig. 6 reveals that the calculated absorption coefficient function agrees qualitatively to the measured one.

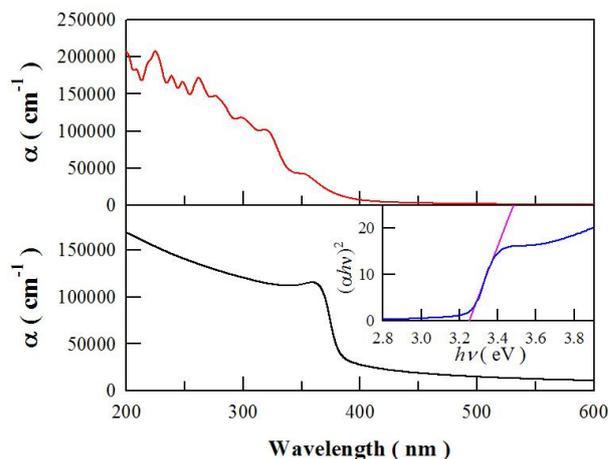


Fig. 6 (a) Calculated absorption spectrum of hexagonal ZnO. (b) Measured absorption spectrum of hexagonal ZnO films grown on the optical quartz substrate.

If a plot of $(\alpha hv)^2$ versus hv forms a straight line, it can normally be inferred that there is a direct band gap which can be measured by extrapolating the straight line to the y axis at $\alpha = 0$. The inset of Fig. 6(b) displays the plot of $(\alpha hv)^2$ against the photon energy hv of the ZnO nanocrystals. As determined from the inset, the band gap of the direct semiconductor ZnO is found to be 3.2496 eV, which agrees well with the widely accepted band gap value of ZnO. It is evident that the calculated band gap of ZnO is accurate although the refractive index and the extinction coefficient are not as good as expected.

4. Conclusion

Using meta-GGA to describe the exchange–correlation functionals, we have performed first-principles calculations in the framework of DFT of the band structures, density of states, dielectric function, refractive index, extinction coefficient and absorption coefficient of ZnO. The calculated bandgap has been shown to be in good agreement with experimental data but the derived optical functions (i.e., the dielectric function, refractive index, extinction coefficient and absorption coefficient) are significantly underestimated in magnitude. In spite of the significant underestimations in the optical properties, we believe that the LDA–PZ based DFT may be a promising tool

for accurately predicting the band structures of ZnO. It is hoped that these findings will stimulate further theoretical and experimental studies into impurity doped ZnO.

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