Use Density Function Theory (DFT) to Investigate the Electrical and Structural Characteristics of Magnesium Oxide (Mgo) in the Wurtzite Phase

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Received: 20/05/2023; Accepted: 01/11/2023; Published : 24/12/2023

Abstract

The ab initio pseudo-potential approach is based on density function theory (DFT), whereby the local density approximation (LDA) according to the Ceperly-Alder (CA) scheme and the generalized gradient approximation (GGA) according to the Perdew-Burke-Ernzerhof (PBE) scheme are employed. This is accomplished by using the Siesta software to look for structural and electrical characteristics of the magnesium oxide (MgO) compound's Wurtzite (B4) phase. In fact, it's a helpful technique for predicting MgO crystal shapes. The lattice constants and the energy gap at zero pressure were found to be consistent with previous theoretical and experimental results; in fact, the calculated structural parameters of this compound are consistent with the available experimental data, so these results can be considered as good predictions. Additionally, the binding energy was confirmed and contrasted with earlier research. The electronic characteristics, particularly the Total Density of States (TDOS) and Partial Density of States (PDOS), further demonstrated the importance of the oxygen atom in the construction of DOS in the vicinity of the Fermi level.

Since the dielectric has an energy gap larger than 3.27 volts, all computed parameters, including the absorption coefficient, reflectivity, extinction, refractive index, imaginary and real parts of the constant, indicate that it may be employed in ultraviolet (UV) applications.

Keywords: Density function theory (DFT), Siesta, MgO, Properties Electronic. Properties Optic.

Tob Regul Sci.™ 2023;9(2): 2087 - 2100

DOI: doi.org/10.18001/TRS.9.2.135

1. Introduction

Recent theoretical or experimental study has shown that the compound MgO has emerged as one of the major oxides. This white solid metal is a major element in the Earth's inner layers, which are located at pressures of around 140 GPa. It is found in the bottom layers of the planet. As a result, in comparison to natural pressure, its structure will alter dramatically. It did, in fact, acquire geophysical significance in this way [1].

MgO is of the II–VI type, meaning that the atoms of magnesium and oxygen are joined by an ionic connection. Given that its energy gap is 7.833 eV, it is one among the fundamental molecules covered in industrial sciences [2]. It may also be used in a variety of applications, including cement, medications, and insulators. It may crystallize in many phases, the majority of which are in the B1, B3, and B4 forms. These phases, which form thin layers on metal substrates, have been studied in a variety of ways [3].

Compared to other oxides, this substance is non-toxic, which is why it was selected for the investigation. Furthermore, it may be used in the production of a few home products. Numerous theoretical and experimental research have been conducted on MgO [4-5]. Chang and Cohen [4] looked for its electrical and structural features for the B1 and B2 phases inside the LDA by utilizing the semi-potential approach. Additionally, the work of Causa et al. [5] is predicated on the application of Hartree-Fock theory to the investigation of the structural characteristics and stability of phases containing MgO.

The cohesive energy of MgO has been investigated in a few earlier investigations. The binding energy is being calculated using two alternative approximations in this investigation. Chang and Cohen [4], for example, estimated the cohesion energy theoretically and empirically, and Jaffe et al. [6] performed the same for MgO and ZnO in different phases, namely: B4, B3, B2, and B1, using the approximations LDA and GGA. The current work's major goal is to investigate the B4 phase of MgO oxide and determine its cohesion energy.

2. Theoretical method

In this case, the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) computer software was used to carry out the simulations. The optimization of the entire system was achieved by adhering to all necessary procedures, including mesh-cutoff, k-point, and lattice optimization, as per density functional theory [7, 8]. All atoms must be completely relaxed during the optimization process in order to get accurate results. Additionally, a Generalized Gradient Approximation (GGA) of Perdew, Burke, and Ernzerhof is employed [9] for an exchange and correlation potential, and we also applied the local density approximation [10. Troullier-Martins norm-conserving pseudo potentials [11] are used to simulate core electrons, while the valence

electron functions are extended in a double zeta polarized basis set [12, 13 of localized orbitals. The real space grid is set at 350 Ry. The structure stays relaxed until the Hellmann-Feynman forces acting on every component of every atom are less than 0.005 $eV_{ı}^{-1}$. As a result, an entirely optimized bulk of MgO was produced, with two Mg and two O atoms.

3. Results and discussion

3.1. Primary cell structure

The lattice constants of magnesium oxide have been confirmed numerous times over the course of several decades [22]. The main cell structure of magnesium oxide that is stable is of the form (B4) wurtzite, a compact hexagon with network constants estimated at α=90.03°, β=90.037°, and γ=119.90° [23]. This compound is characterized by the group P63mc.

Two magnesium atoms occupy the following positions (0.0.0), (1/3.2/3.1/2), for every four atoms in a primary cell of magnesium oxide. Meanwhile, oxygen atoms occupy the following gravitational positions (1/3. 2/3. μ), (0. 0. μ), where ε is the internal variable of the Wurtzite shape, which determines the length of the bonds between

magnesium and oxygen. μ is therefore given as the next one:

$$\mu = \left(\frac{1}{4} + \left(\frac{c^2}{3.a^2}\right)\right) \quad (1)$$

The siesta program, which was utilized to determine the major cell constants for MgO, is the basis for the computations in this paper. Table 1 tabulates the results in this regard.

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Table 1 presents a comparison between theoretical and actual data for the primary cell constants of magnesium oxide.

	a (Å)	c (Å)	μ (Å)	c/a
Our Results GGA LDA	3.327 3.288	5.025 5.004	1.0117 1.2205	1.5103 1.5219
Theoretical works by GGA method	3.308 [16] 3.281 [17] 3.310 [18] /	5.074 [16] 5.136 [17] 5.123 [18] /	0.386 [16] 0.393 [17] 0.391 [18] /	/ / 1.547 [18] 1.530 [19]
Theoretical works by LDA method	3.252 [16] 3.322 [14] 3.249 [18] 3.320 [19] 3.322 [20] 3.169 [21] /	5.027 [16] / 5.277 [18] 5.056 [19] / 5.175 [20] /	0.391 [16] 0.391 [22] 0.391 [26] 0.386[19] 0.392 [19] 0.375 [21] 0.393 [22]	/ 1.546 [14] 1.547 [18] 1.565 [19] / 1.536 [21] 1.506 [22]

	3.278 [23]	5.062 [23]	/	/
experimental work	3.283 [19]	5.095 [19]	0.388 [19]	1.552 [19]

We were able to determine the initial cell constants and get the values of 3.327 Å for constant a and 5.025 Å for constant c by utilizing Siesta software and density function theory (DFT). Considering that the structure is hexagonal, we will discover that a = b in any situation. As a result, it should be highlighted that these findings strongly concur with the practical and theoretical findings included in the preceding references table [16–23].

Furthermore, by comparing the obtained values with the experimental values that were used as a reference, the error ratio was calculated. This allowed us to determine that, in the case where the GGA approximation was used, the error value was estimated to be 1.34 percent for the constant a and 1.37 percent for the constant C. And to discover that, if we employ the LDA approximation, the error value is 0.15 percent for the constant a and 1.79 percent for the constant C, therefore the computed error levels appear tiny to us overall, indicating that the calculating process is sensible and logical.

3.2. Energy of Magnesium Oxide (MgO)Formation:

The formation energy of MgO was calculated for each pair (Mg-O), with the following relationship:

$$E_C = E_T[MgO] - E_T[Mg] - E_T[O] \qquad (2)$$

Whereas:

ET(MgO): total energy of the MgO in the solid state, ET(Mg): total energy of the free Mg atom, ET(O): total energy of the free O atom, Ec: formation energy.

The results of calculating the formation energy of MgO are shown in Table 2:

Table 2: The pair's formation energy (Mg-O).

Formation energy of the pair (Mg-O)	
Our results	Another theory's results
GGA (5.7694) eV	GGA (7.692) eV [6]
LDA (5.8120) eV	LDA (9.769) eV [6]

GGA(11.5389) eV/pair	GGA (10.05) eV/pair [24]
LDA(11.6240) eV/pair	GGA (10.85) eV/pair [21]
	Experimental results 7.52 eV[25]

Using LDA, the value of MgO production to bind each pair (Mg-O) was 5.8120 eV, whereas GGA yielded a value of 5.7694 eV. Both outcomes closely resemble the experimental findings made at the work [17].

1.3. Electronic properties of the compound

1.3.1. Structure of energy bands

To determine the electrical characteristics of the substance, the Brillion region is selected for primary structural research. The Brillion zone related with the hexagon is seen in the example. It is important to remember the characteristics studied in this region may later be applied to MgO.

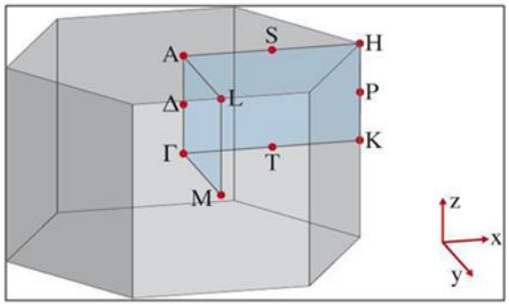

Fig. 1. Brillion region of a Wurtzite crystal.

The energy gap of MgO was found using DFT and GGA. This approach has also been used since it is one of the most effective ways to examine the electrical structures of various materials. For the previously determined lattice constants (a=3.327Å, c=5.025Å, β=90.037°, α=90.03°, and γ=119.90°), the energy bands structure of MgO was computed.

The structure of energy bands of MgO was calculated as shown in figure 2:

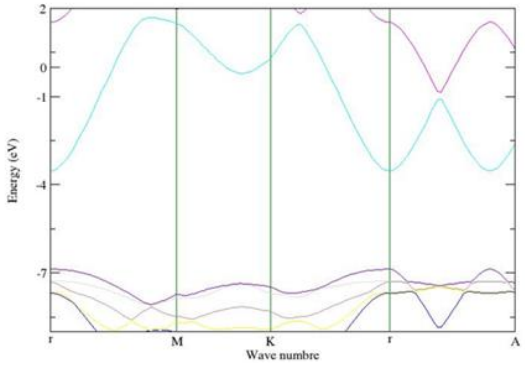

Fig. 2. Energy band structure of the Wurtzite phase MgO.

The previous image shows that the conduction band's lowest peak and the valence band's highest peak are on the same line, passing through point K. This explains why the predicted direct gap of MgO is 3.27 eV.

1.3.2 Density of Electronic States:

Total Density of State (TDOS) and Partial (PDOS) of MgO compound are analyzed using the GGA and LDA, as shown in Figures 3 and 4, respectively, in order to ascertain the origin of the existence of states that formed both valence and conduction bands and to comprehend the nature of the interactions between atoms of the studied compound. values are still a lower estimate of the actual energy gap values.

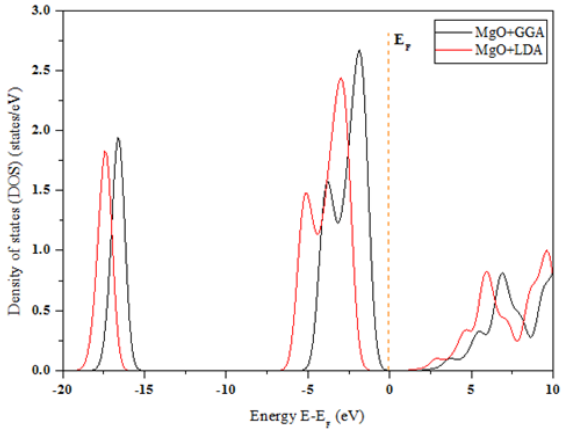

Fig. 3. Total density of state (TDOS) of MgO with GGA and LDA.

Figure 3 illustrates how the computed TDOS exhibits high MgO values at the Fermi level with GGA and LDA. When using GGA instead of LDA, the TDOS value of MgO is greater. This indicates that there are many electrons in the valence band.

We see that at the Fermi level, the maximum TDOS of MgO determined by GGA is 2.8 states/eV, with a lower value determined by LDA estimated at 2.5 eV in the same area. The TDOS calculated at 1.0 state/eV in the energy field stretching from [6-7,5] eV is shared by the two almost similar TDOS curves of MgO with GGA and LDA in the conduction region around the Fermi level.

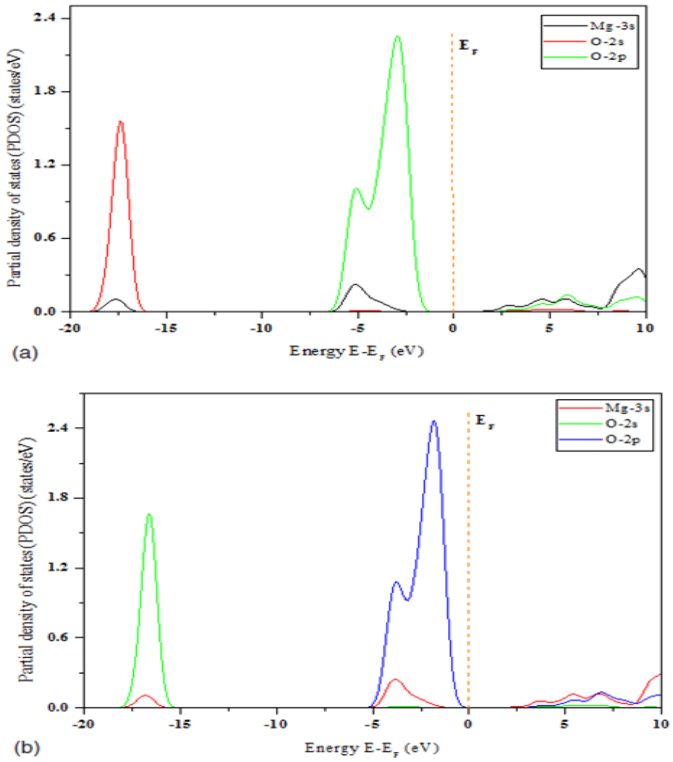

Fig. 4. Partial density of state (PDOS) of MgO with (a) GGA and (b) LDA.

The PDOS of the MgO compound will be computed and thoroughly discussed in this study in order to comprehend the motion of electrons that are near the Fermi level. Prior to doing this, we must understand the PDOS of Mg and O, which are important in forming the TDOS of MgO in its solid state. The PDOS of MgO by GGA is displayed in Figure 4-a, while the PDOS of MgO by LDA is displayed in Figure 4-b.

We may conclude that the basis of the 2p orbital of the O element and the 3S orbital of the Mg element is what causes the appearance of DOS values in the valence band area since Figure 4 shows that the two curves appear to have the same overall shape. Consequently, the p orbital of the O element and the s orbital of the Mg element are accountable for DOS in the valence band area. We also see the appearance of two stations close to the Fermi level: one for O-2p at -2.5 eV and another for Mg-3s at -3.5 eV.

In the event that MgO is subjected to external stimulation, such as light, the nearly nonexistent O-2s station aids in the quick transfer of electrons from the valence band to the conduction band. The conduction band is where PDOS peaks were recorded, and the oscillatory values at the Mg-3s, O-2p, and O-2s stations appear to be the same.

3.2. OPTICAL PROPERTIES

Finding out a material's optical constant values over a broad range of wave lengths is crucial for designing and producing optical components and optical pulses with a variety of technological applications. This is why studying a material's optical properties is important.

3.2.1. ABSORPTION COEFFICIENT

It is the decreasing ratio of incoming radiation energy in the spectrum with regard to the unit distance in the direction that the wave propagates through the medium. The energy of the incoming photons and the semiconductor's characteristics determine the absorption coefficient. The values of the absorption coefficient and its equation can be used to determine the kind of electronic transitions, whether direct or indirect:

$$\alpha = \frac{4\pi K}{\lambda} \qquad (3)$$

where λ is the wave length (cm), k is the coefficient of extinction, and α is the absorption coefficient.

Figure 5 displays the values of the adsorption coefficients for MgO, which were computed using approximations of GGA and LDA.

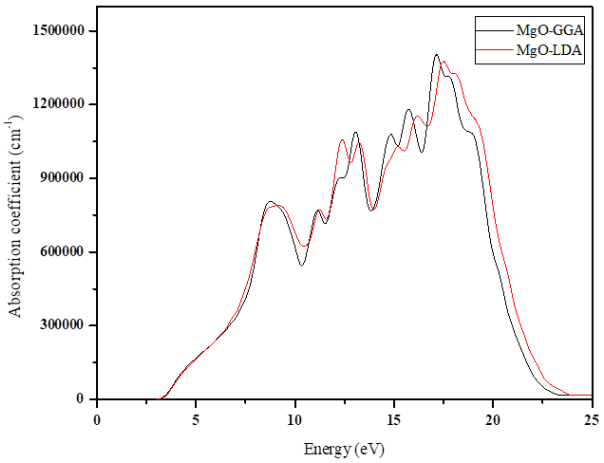

Fig. 5. Absorption Coefficient of MgO.

The variation in the absorption coefficient on the MgO compound with respect to the incoming photon's energy is seen in Figure 5. The graphic makes it evident that when light photon energy increases, the absorption coefficient typically starts to rise gradually. Additionally, four peaks with centers at 8.25 eV, 13.5 eV, 16.5 eV, and 18.7 eV are recorded beyond the absorption threshold, which is measured at 3,2 eV. At these energies, these peaks suggest that there may be direct electronic transitions between the valence and conduction bands.

As a result, we discover that the compound is regarded as opaque in the [3.2–22.5] eV domain but transparent in the active fields [0-3.2] eV and [22.5–25] eV. This suggests that varied optical characteristics in this material are caused by changes in the incident photons' energy. This outcome is nearly complete [26].

3.2.2. OPTICAL CONDUCTIVITY

It is a physical characteristic that links the current density to the electric field at a general frequency. It is closely associated with the dielectric constant, which is represented by the following equation:

$$\sigma(\omega) = \frac{J(\omega)}{E(\omega)} \qquad (4)$$

Where σ is optical conductivity (Sm/m), J is current density (A/m^2) and E is electric field (N/C)

The photoconductivity values for MgO were calculated with approximations of GGA and LDA, the results are as shown in Fig 6.

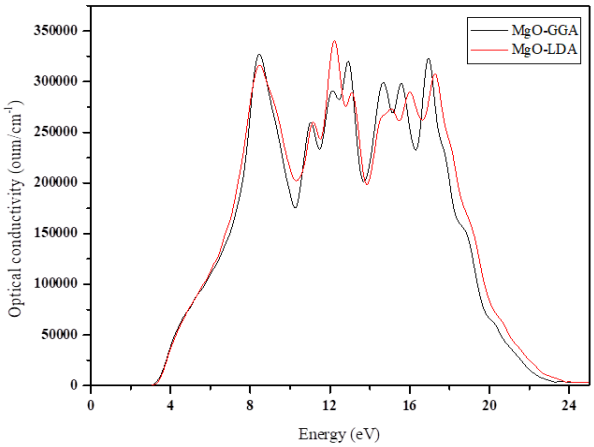

Fig. 6. Optical Conductivity of MgO.

Using the GGA and LDA approximations, Figure 6 illustrates how photoconductivity changes as a function of photon energy falling on the MgO compound. We found that no optical conductivity value was recorded in the range of 0 eV to 3.2 eV because it falls within the forbidden range, and that the photoconductivity value increases in the range of 6 eV to 20 eV as three distinct peaks at 8 eV, 13 eV, and 17 eV differentiate in this area, corresponding to the photoconductivity value in the range of 325,000 ohm/cm-1.Although a notable decline in photoconductivity was seen once the energy value attained 20 V, these outcomes are in line with the findings of the study [27]. The greatest absorption value of the MgO compound enables its application in optoelectronics and optical energy compounds, as inferred from the examination of the absorption and optical conductivity curves.

3.2.3. EXTINCTION COEFFICIENT

The degree of attenuation in the electromagnetic beams' intensity as they travel through the material medium is known as the extinction coefficient. The following formula, which has to do with the absorption coefficient, may be used to get the extinction coefficient.

$$k = \frac{\alpha\lambda}{4\pi} \qquad (5)$$

Where k: is extinction coefficient, α is absorption coefficient (cm^{-1}) and λ is wave length (cm). The value of the extinction coefficient for MgO was calculated by approximating GGA and LDA as shown in Figure 7.

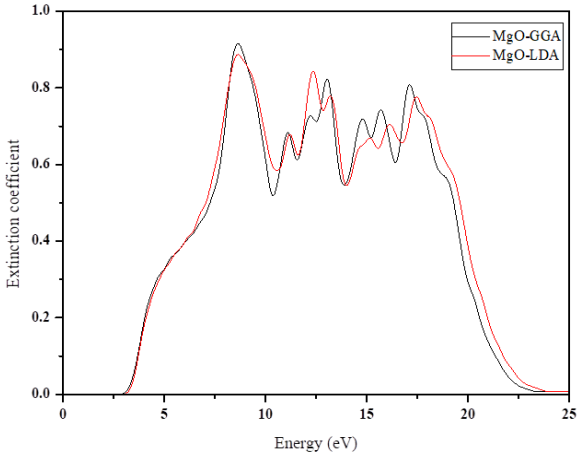

Fig. 7. The Extinction Coefficient of MgO.

The extinction coefficient changes are depicted in Figure 7 as changes in energy using the GGA and LDA approximations. The figure makes it evident that the extinction coefficient curve behaves almost similarly to the absorption coefficient curve (α) because of their relationship to the previous one. In order to do this, we found that the extinction coefficient was present in the forbidden range in the range from (0 to 3.2) eV, and in the range from (3.2 to 18) eV, no value was recorded. Three distinct peaks at 7.8 eV, 12.5 eV, and 17 eV with extinction coefficient values of (0.9), (0.8), and (0.78), respectively, represent the increasing value of the extinction coefficient. These peaks are consistent with the findings [26] and suggest the potential of direct electronic transitions between the valence and conduction bands at these energies.

3.2.4. DIELECTRIC CONSTANT

The medium becomes polarized when light and charges interact because the process of absorbing a substance's energy causes the medium to become charged; this polarization is explained by the dielectric constant. which is known by the following relationship:

$$\varepsilon = \varepsilon_r - i\varepsilon_i \qquad (6)$$

Where ε is complex dielectric constant, ε_r is real part of the dielectric constant and ε_i is imaginary part of the dielectric constant.

The values of the dielectric constant in its imaginary and real parts for the MgO were calculated by approximating GGA and LDA as respectively presented in Figure 8 and Fig 9.

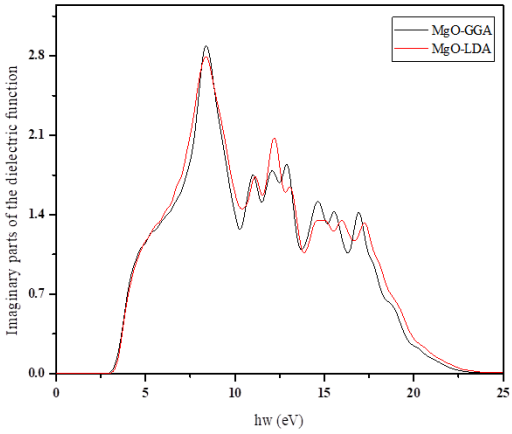

Fig. 8. The Imaginary Part of the dielectric constant of MgO.

Using the GGA and LDA approximations, Figure 8 illustrates the shift in the imaginary component of the dielectric constant (ε_i). In order to do this, we found that when employing GGA and LDA, the curves for the imaginary component of the dielectric constant are essentially the same. Additionally, we observed that the value of (ε_i) is zero between 0 and 3.2 eV before progressively increasing to its maximum value at (2.9) at 7.6 eV. With two successive peaks less than the first peak, corresponding to 2.1 and 1.4 and this at energies of 12.2 eV and 17 eV, respectively, to record a decrease in the imaginary part of the dielectric constant in the form of oscillations; these results are similar to what was achieved in [26]. The two curves then gradually decrease to the value of 22.5 eV. We determine that the optical gap has a value of 3.2 eV.

3.2.4.1. THE RRAL PART OF THE DIELECTRIC CONSTANT

The real part of the dielectric constant values for MgO was calculated using GGA and LDA approximations and the results are represented as in Fig 9.

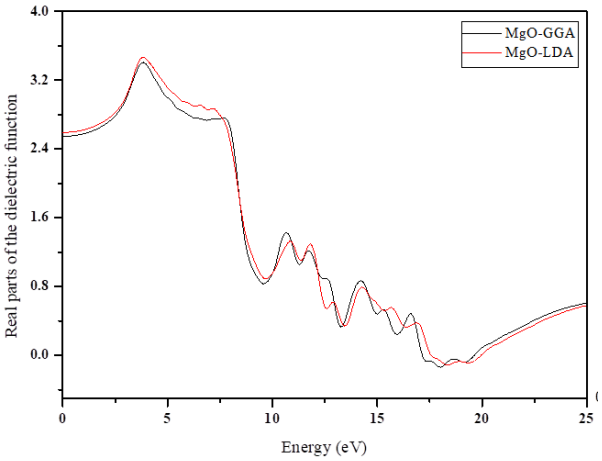

Fig. 9. The real part of the dielectric constant of MgO.

Figure 9 represents the changes in the real part of the dielectric constant (ε_r) as a function of the incident photon energy of the MgO compound using the GGA and LDA approximations. The

figure shows that the curves of the real part of the dielectric constant are almost similar to the curves of the refractive index with the approximations of GGA and LDA, due to the nature of the relationship between them with the previous relationship and this similarity is caused by the dependence on calculating the values of the real part of the dielectric constant on (n_{02}) values more than (n_{02}) values (n_{02}) (k_{02}) This is because (k_0) values are very few compared to (n_0) values where the effect of extinction coefficient is weak especially after squaring. Here, we observed that the value of (ε_r) starts from (2.6) at 0 eV and then increases to a peak (3.6) at 4.8 eV and then gradually decreases until it reaches zero.

3.2.6. REFRACTIVE INDEX

It is the ratio between the speed of light in free space and its speed in the matter, and the refractive index can be found according to the following equation:

$$n_0 = \left[\left(\frac{1+R}{1-R}\right)^2 - (k_0^2 + 1)\right]^{\frac{1}{2}} + \frac{1+R}{1-R} \qquad (7)$$

The refractive index values for MgO were calculated using the GGA and LDA approximations as shown in Figure 10.

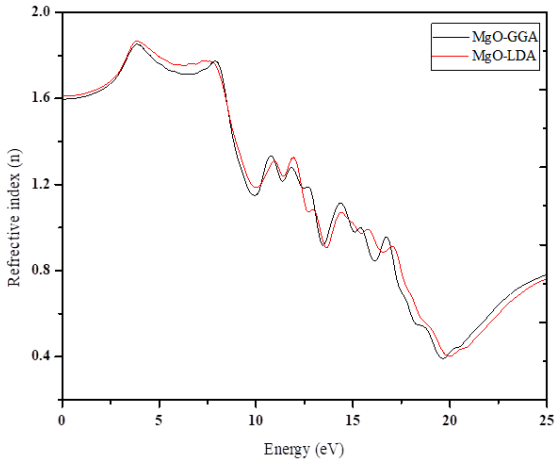

Fig. 10. Refractive index of MgO.

The refractive index is only significant in the non-absorbed region that lies under the energy gap, as shown by Figure 10, which expresses the refractive index in terms of the incident photons. The static refractive index (n_0) for MgO is (1.6), after which the refractive index is increased until it becomes (1.9) at an energy value of 4.5 volts, and the presence of small and decreasing vibrations is recorded to reach the value zero, which is fully consistent with the work [27].

Conclusion

The Wurtzite (B4) phase MgO compound, which has excellent stability in comparison to other phases, allowed us to determine the principle state characteristics using density function theory, the Generalized Gradient Approximation, and the Local Density Approximation. The DFT

method and the use of the Siesta program are among the most efficient ways to predict the general properties of the principle state of MgO compound because of the strong compatibility between the results of our calculations regarding the binding energy of MgO and the results of previous theoretical and experimental work regarding the calculation of primary cell constants for the Wurtzite phase. Furthermore, our calculations indicated that the orbital Mg-3s makes a less contribution to the construction of the PDOS values close to the Fermi level than does the O-2p orbital. Our findings also support the predicted 3.27 eV direct gap for MgO.

The compound's behavior as a semiconductor with an energy gap of 3.27 eV was confirmed by the value of the imaginary part of the dielectric constant. This was further supported by the results of the real part of the calculated dielectric constant, where the optical properties computed in the GGA approximation are more accurate than those in the LDA approximation, and the absorption, extinction, reflectivity, and refractive index indicate that MgO is a good candidate for applications that fall within the UV range.

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