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Structural and optical properties of Wurtzite phase MgO: first principles calculation

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The pseudo ab initio ability is based on density function theory (DFT), use of generalized gradient approximation (GGA), local density approximation (LDA).We use of the Siesta symbol for the first time in studying this particular compound and the wurtzite phase that enabled us to find the structural and optical properties of MgO in its crystal structure (B4) wurtzite. Where the structural results indicated that the wurtzite phase has lattice constants very close to what was found previously in applied studies, and all the calculated properties such as absorption coefficient, reflectivity, extinction, refractive index, imaginary and real part of the constant show that the dielectric has an energy gap greater than 3.27 eV, meaning that it can be used in applications in the ultraviolet (UV) region, and all properties calculated by approximation (GGA) give slightly better results than the use case approximation (LDA).The results obtained when we study the compound MgO wurtzite are a reference for further theoretical and experimental studies.

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1. Introduction

The II-VI semiconductor type is characterized by a large energy gap, which gave it an important role in the field of electronics and photoelectrons. This is what it achieves for both lasers and light-emitting diodes (LDs, LEDs) [1], especially for blue/green light emitters [2]. Consequently, this is a result of the transfer of electronic charge from group II to elements of group VI, where ionic bonds become more effective as a result between groups II and VI. For this purpose, the process of combining binary and hexa-compounds from the periodic table enables us to obtain new materials with new physical properties such as energy gap, lattice constants, dielectric constant...etc, which enable us to meet the requirements of modern day devices

The MgO compound has become one of the most interesting oxides in recent years due to the large number of researches that have been conducted on it, both theoretical and experimental. In fact, the bulk of it crystallizes in several stages, namely B1 and B4. In this regard, several studies have also been carried out in order to study the thin layers as well as the primary cell structure of the MgO complex, which is localized on different metal substrates [3-7]. Due to its large energy gap, it is used as a substrate and catalyst [8-10], as well as in the production of superconductors, thermal shock transformers, in the formation of AC protective layers [11-12], plasma display panels, and spintronic devices.

In this study, we focused on studying the structural and optical properties of the B4-phase MgO compound, where we used the density function theory (DFT) [13], using the Siesta code [14]. The new aspect of the current study is based on finding the structural and optical properties of the compound MgO (B4) using simulations and using the Siesta code to verify them, which was not used before in previous studies of the aforementioned compound. Therefore, after the summary and the introduction, the rest of the research is divided as follows: Section 2 is a brief overview of the used theoretical calculation method, and Section 3 is concerned with the summaries and the

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discussions of the findings obtained from structural and optical properties. Furthermore, everything that has been achieved in this research paper is summarized under the heading of conclusion in section 4.

2. Theoretical method

Here we performed simulations by using a computational program called Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA). This is based on density functional theory [15-16] whereby the whole system was optimized by following all essential steps such as mesh-cutoff, k-point, lattice-optimization…etc. For correct results, all atoms must remain fully relaxed while performing the optimization. Moreover, for an exchange and correlation potential; a Generalized Gradient Approximation (GGA) of Perdew – Burke – Ernzerh of is used [17] and we also used the local density approximation [18]. Core electrons are modeled with Troullier–Martins norm-conserving pseudo potentials [19] the valence electrons functions are expanded in double zeta polarized basis set [20-21] of localized orbitals and the real space grid is set to be 350 Ry. Until the Hellmann–Feynman forces acting on all components of each atom are smaller than 0.005 eVÅ^{-1}, the structure remains relaxed. This yielded a fully optimized MgO bulk which contained 2 Mg and 2 O atoms.

3. Results and discussion

3.1. Primary cell structure

The lattice constants of MgO have been verified many times over several decades [22], the primary cell structure of stable MgO is of the form (B4) wurtzite, which is the compact hexagon that is characterized by the group P63mc and network constants estimated at a=b= 3.283 Å, c = 5.095 Å, α=90.03°, β=90.037° and γ=119.90° [23].

Each primary cell of MgO oxide consists of four atoms, and every two magnesium atoms occupy the following positions (0.0.0), (1/3.2/3.1/2) while we find that oxygen atoms occupy the following gravitational positions: (1/3. 2/3. μ), (0. 0. μ) where μ is the internal variable of the wurtzite shape, which determines the length of the bonds between magnesium and oxygen, so μ is given as next one:

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

The calculations in this work depend on the siesta program, which was used to calculate the primary cell constants for MgO. In this respect, the results are tabulated in table 1.

Table 1. Primary Cell Constants of MgO and their Comparison with theoretical and experimental results.

	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 [24] 3.281 [25] 3.310 [26] /	5.074 [24] 5.136 [25] 5.123 [26] /	0.386 [24] 0.393 [25] 0.391 [26] /	/ / 1.547 [26] 1.530 [27]
Theoretical works by LDA method	3.252 [24] 3.322 [22] 3.249 [26] 3.320 [27] 3.322 [28] 3.169 [29] / 3.278 [31]	5.027 [24] / 5.277 [26] 5.056 [27] / 5.175 [29] / 5.062 [31]	0.391 [24] 0.391 [22] 0.391 [26] 0.386 [27] 0.392 [28] 0.375 [29] 0.393 [30] /	/ 1.546 [22] 1.547 [26] 1.565 [27] / 1.536 [29] 1.506 [30] /
Experimental work	3.283 [27]	5.095 [27]	0.388 [27]	1.552 [27]

Using density function theory (DFT) and using Siesta software, we were able to calculate the initial cell constants and then find the value: 3.327 Å for constant a and the value: 5.025 Å for constant c. Taking into account that the structure is hexagonal, we will find that in all cases a = b. Accordingly, it is noted that these results are in great agreement with the theoretical and applied results mentioned in the previous references table [24-31]. In addition, the error ratio was calculated for the obtained values, by making a comparison with the experimental values taken as a reference, to find that the error value was estimated at 1.34 % for the constant a and the value of 1.37 % for the constant c in the case if we use the approximation GGA, And to find that the error value is 0.15 % and that for the constant a and the value of 1.79 % for the constant c if we use the LDA approximation, then on the whole the calculated error values to us seem small, which suggests that the method of calculation is logical and reasonable.

3.2. Optical properties

The importance of studying the optical properties of materials lies in obtaining information about the values of the optical constants of the material in a wide range of wave lengths, as this information is used in the design and manufacture of optical pieces and optical pulses with different technological uses.

3.2.1. Absorption coefficient

It is the decreasing ratio in the spectrum of the incident radiation energies with respect to the unit distance towards the direction of propagation of the wave within the medium. The absorption coefficient depends on the energy of the incident photons and the properties of the semiconductor. The nature of the electronic transitions, whether direct or indirect, can be known from the values of the absorption coefficient, its equation from the figure:

$$\alpha = \frac{4\pi K}{\lambda} \tag{2}$$

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

The adsorption coefficient values for MgO were calculated with approximations of GGA and LDA, and they are shown in Fig. 1.

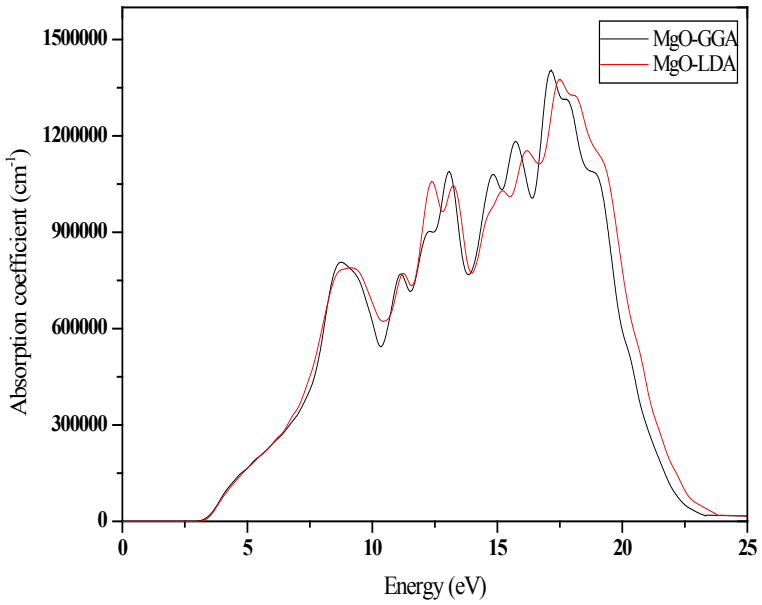

Fig. 1. Absorption coefficient of MgO.

Figure 1 shows the change in the absorption coefficient as a function of the energy of the incident photon on the MgO compound. It is clear from the figure that the absorption coefficient generally begins to increase gradually with the increase in the energy of light photons. In addition, the absorption threshold is measured at 3.2 eV, followed by four peaks centered at 8.25 eV, 13.5 eV, 16.5 eV, and 18.7 eV, these peaks indicate the possibility of direct electronic transitions between the valence band and conduction bands at these energies. Therefore we find in the active fields [0-3.2] eV and [22.5-25] eV, the compound is considered transparent, while in the [3.2-22.5] eV domain, the compound is considered opaque. This indicates that the change in the energy of the incident photons leads to different optical behaviors in this material. This result is close to work [32].

3.2.2. Optical conductivity

It is a physical property that binds the current density to the general frequency electric field and is closely related to the dielectric constant known as the following equation:

$$\sigma(\omega) = \frac{J(\omega)}{E(\omega)} \tag{3}$$

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. 2.

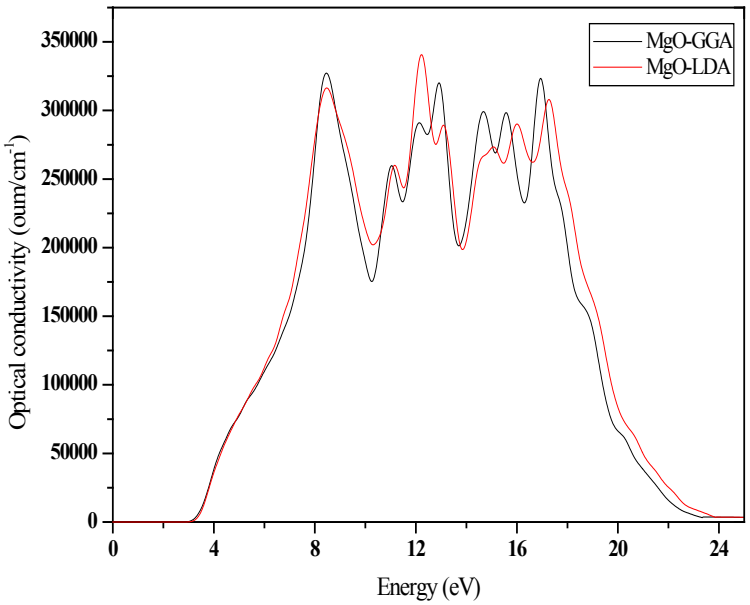

Fig. 2. Optical conductivity of MgO.

Figure 2 represents the photoconductivity changes in terms of the energy of photons falling on the MgO compound using the GGA and LDA approximations, we noticed in the range from 0 eV to 3.2 eV that no optical conductivity value was recorded because it is in the forbidden range, and in the range from 6 eV To 20 eV, the photoconductivity value increases as 3 different 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}. While a significant decrease in the photoconductivity value was recorded after the energy value reached 20 eV, and these results are similar to what was achieved in the work [33]. We conclude from the analysis of the absorption and optical conductivity curves that the MgO compound has a maximum absorption value that allows it to be used in optoelectronics and optical energy compounds.

3.2.3. Extinction coefficient

The extinction coefficient is defined as the amount of attenuation in the intensity of the electromagnetic rays when they pass through the material medium. The extinction coefficient can be calculated based on the following equation, which is related to the absorption coefficient.

$$k = \frac{\alpha\lambda}{4\pi} \tag{4}$$

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 Fig. 3.

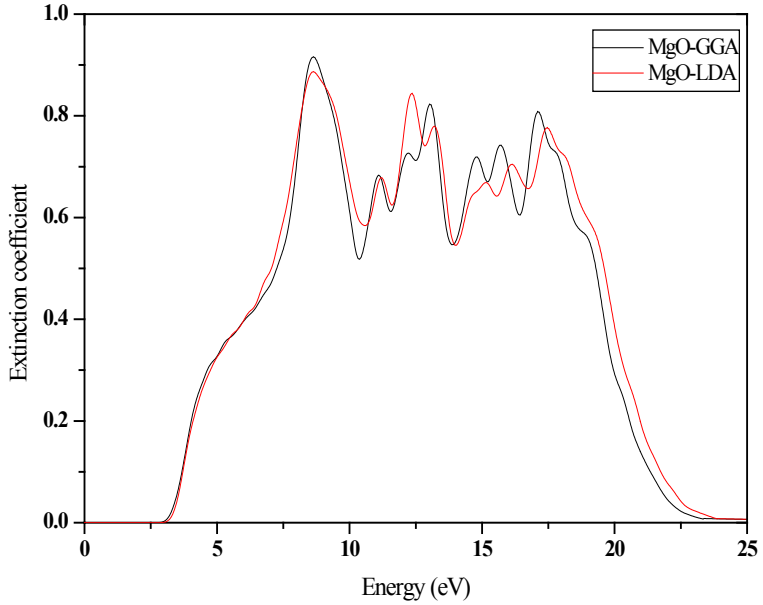

Fig. 3. Extinction coefficient of MgO.

Figure 3 represents the changes in the extinction coefficient in terms of energy using the GGA and LDA approximations; it is clear from the figure that the nature of the extinction coefficient curve is almost similar to the behavior of the absorption coefficient curve (α) due to the nature of their relationship with the previous one. To this end, we observed that in the range from (0 to 3.2) eV there was no recorded value of the extinction coefficient due to its presence in the prohibited range, and in the range from (3.2 to 18) eV, the value of the extinction coefficient increases and this is embodied in 3 different peaks at 7.8 eV, 12.5 eV, and 17 eV at the value of the extinction coefficient is 0.9, 0.8 and 0.78 respectively. These peaks indicate the possibility of direct electronic transitions between the valence and conduction bands at these energies, and it is in agreement with what was reached [32].

3.2.4. Dielectric constant

When the interaction between the light and the charges of the medium is the result of the process of absorbing the energy of a substance, the interaction results in the polarization of that medium, and this polarization is described by the dielectric constant, which is known by the following relationship:

$$\varepsilon = \varepsilon_r - i\varepsilon_i \tag{5}$$

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.

According to the relationship between the dielectric constant and the refractive index.

$$\varepsilon = N^2 \tag{6}$$

We can find the real and imaginary dielectric value after making up for the N value, so that we can get:

$$(n_0 - iK_0)^2 = \varepsilon_r - i\varepsilon_i \tag{7}$$

By solving this equation we get:

$$\varepsilon_r = n_0^2 - K_0^2 \tag{8}$$

$$\varepsilon_i = 2n_0K_0 \quad (9)$$

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 Fig.4 and Fig. 5.

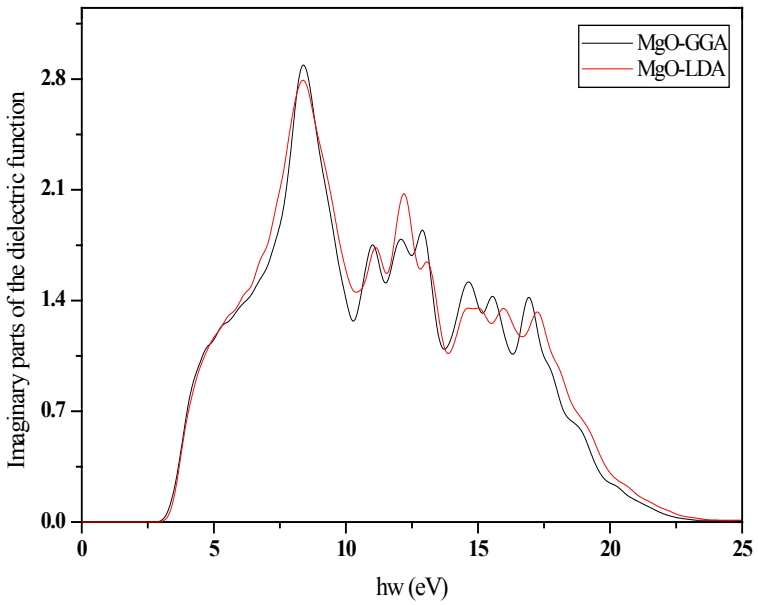

Fig. 4. Imaginary part of the dielectric constant of MgO.

Figure 4 represents the change of the imaginary part of the dielectric constant ε_i using the GGA and LDA approximations. To this end, we observed that the curves for the imaginary part of the dielectric constant with using GGA and LDA are generally identical. We also noticed that the value of (ε_i) is zero from (0 to 3.2) eV and then gradually increases until it reaches its maximum value 2.9 at 7.6 eV. To record a decrease in the value of the imaginary part of the dielectric constant in the form of oscillations, 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, then the two curves gradually decrease to the value of 22.5 eV and these results Similar to what was achieved in [32]. We conclude that the value of the optical gap is 3.2 eV.

3.2.4.1. The real 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. 5.

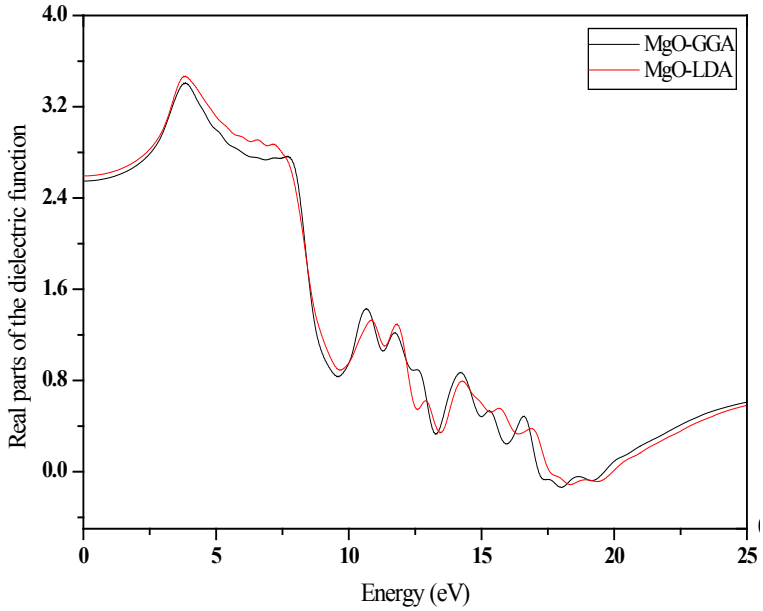

Fig. 5. Real part of the dielectric constant of MgO.

Figure 5 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_0^2 values more than n_0^2 values (n_0^2. k_0^2). 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.

3.2.5. Reflection

The reflectivity (R) is defined as the ratio between the intensity of the radiation reflected from the membrane in a particular direction to the original intensity of the radiation falling on it whereby it is presented in the form of the following equation:

$$R = [(n_0 - 1)^2 + k_0^2/(n_0 + 1)^2 + k_0^2] \quad (10)$$

Where R is reflection coefficient, n_0 is refractive index and k_0 is extinction coefficient.

The reflectance coefficient values for the MgO compound were calculated using the GGA and LDA approximations as shown in Fig. 6.

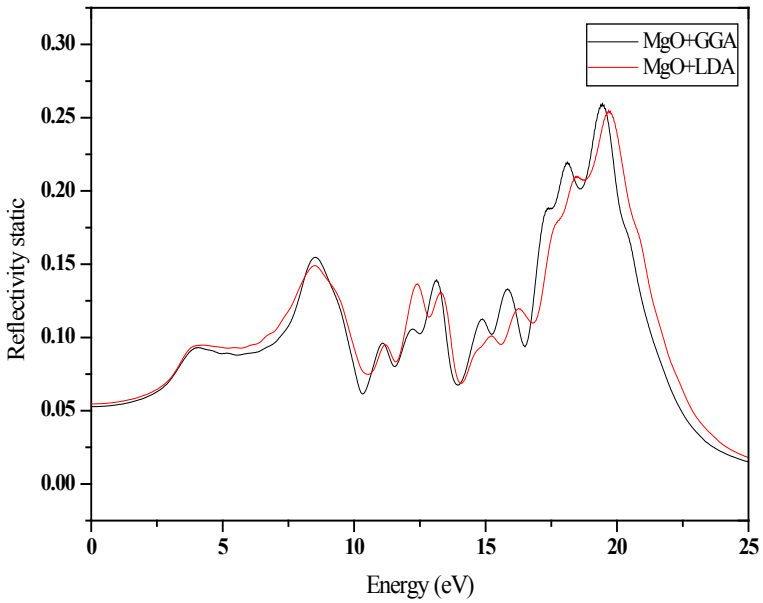

Fig. 6. Reflectivity of MgO.

Figure 6 represents the changes in the reflection coefficient in terms of energy. Accordingly, we note that the reflection curves if we use GGA and LDA approximations are generally consistent with each other. We also observed that the reflectivity increases with the energy of the incident photons in both the GGA and LDA approximations, starting from a value of 0.05 at 0 eV. So that it gradually increases in the form of oscillations and reaches two peaks, the first at 0.15, corresponding to the energy of 8 eV, and the second peak at 0.125, which corresponds to the energy of 12.5 eV, to continue increasing until the peak reaches 0.26 at the energy of 20 eV, to decrease thereafter. This is in good agreement with the work [33]. Therefore, we conclude that MgO has a high reflectivity that makes it used in coatings and optical device applications.

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:

$$n_0 = \left[\left(\frac{1+R}{1-R}\right)^2 - (k_0^2 + 1)\right]^{\frac{1}{2}} + \frac{1+R}{1-R} \tag{11}$$

The refractive index values for MgO were calculated using the GGA and LDA approximations as shown in Fig. 7.

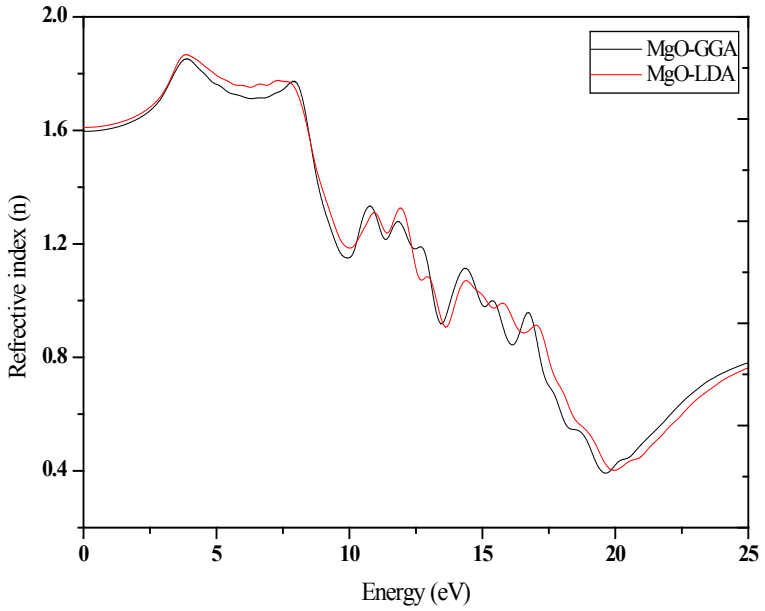

Fig. 7. Refractive index of MgO.

From Figure 7, which expresses the refractive index in terms of the incident photons, the refractive index is important only in the non-absorbed region that lies under the energy gap, and the value of the static refractive index n_0 for MgO is 1.6 after which the refractive index is increased until the value becomes 1.9 at an energy value of 4.5 eV, and the presence of small and decreasing vibrations is recorded to reach the value zero, and this is fully consistent with the work [33].

4. Conclusion

Based on the calculations made according to the density function theory (DFT), and the use of the Siesta program, as well as the comparison of the results obtained through the approximation (GGA) and (LDA), whether structural or optical, to study the compound MgO with wurtzite phase (B4), it was concluded that :

The structural results indicated that the network constants of the primary cell in the case of Bulk gave results very close to what was reached in previous theoretical and experimental studies, and the use of approximation (GGA) shows results more accurate and close to what was reached in previous theoretical and experimental studies.

The value of the imaginary part of the dielectric constant confirmed that the compound behaves like a semiconductor with an energy gap of 3.27 eV, and this was also confirmed by the results of the real part of the calculated dielectric constant, where the absorption, extinction, reflectivity and refractive index indicate that MgO is a good candidate for applications that it is within the UV range, in addition the results of the optical properties computed in the GGA approximation are more accurate than in the LDA approximation.

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