Concentration effect on the vibrational and electronic properties of $Mg_XZn_{7-X}O_7$ wurtzoids nanostructure via DFT

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In the present work, the ternary compound $Mg_xZn_{7-x}O_7$Wurtzoid with variable Zn and Mg contents was analyzed using density functional theory with B3LYP 6-311G**basis set. The electronic and vibrational properties of $Mg_xZn_{7-x}O_7$ wurtzoids, were investigated, including energy gaps, bond lengths, spectral properties, such like infrared spectra and Raman. IR and Raman spectra were compared with experimental longitudinal optical modes frequency results. The theoretical results agree well with experiments and previous data. It has been found that the energy gap is increasing with the increased Mg concentration, and that the longitudinal optical position exposes a UV shift movement with an increase in the concentration.

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Keywords: MgZnO nanostructure, Concentration, band gap, Ab initio method, DFT

1. Introduction

II-VI broadband semiconductor materials expand major applications in optoelectronics and electronics, especially devices that emit visible light in the short wavelength range. This is primarily according to the direct band gap and appropriate energy band gap [1-5]. From these materials, ZnO is one of the most promising semiconductors for device applications. This is mainly according to the large energy gap, and the large binding energy of the free excitons [6-10]. MgO is also the II-VI semiconductor material used in many technical applications, which is a chemically stable and physical solid in high temperatures. This material has low electrical conductivity and high thermal conductivity [11-16]. Recently, the research on $Mg_xZn_{7-x}O_7$ ternary nanocrystals has attracted the attention of many scholars and experts. It offers direct band gap properties, has high absorption coefficients in the blue and ultraviolet regions, and may be a useful semiconductor because of its large band gap properties between MgO and ZnO. For example, the compositionally tunable band gap width and size can be tuned from (3.3-7.8 eV) [8,9]. $Mg_xZn_{7-x}O_7$is a wide-band gap semiconductor material with widely tunable gap energy derived from MgO and ZnO alloys. Create the alloys with Mg, in particular, sings the material and makes it useful for biomedical applications, especially when used as nanoparticles [17,18]. Pulsed laser deposition is used to create thin films of $Mg_xZn_{7-x}O_7$, and their photoluminescence peak and optical band gap can be tuned to the higher energy side. [19]. ZnO is crystallized in the wurtzite structure [20]. But MgO tends to crystallize in the structure of rock salt [11-16]. Because the formation energy of the ZnO-MgO alloy structure in the wurtzite form has been reported to be quite comparable, the $Mg_xZn_{7-x}O_7$ alloy adopts the wurtzite structure. [21].

Recently, wurtzite-$Mg_xZn_{7-x}O_7$ alloys have received extensive attention as candidates for blue and UV applications in optoelectronic devices. ZnO is a wide-band gap semiconductor with a direct band gap of about 3.3 eV. When Zn atoms are replaced by Mg atoms with similar ionic radii, the band gap becomes wider, allowing the construction of quantum wells and super-Lattices. [22]

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The sphalerite GaAs/$Al_xGa_{1-x}As$ system exhibits similar behavior and forms the basis of many modern optoelectronics. [23] Recent trends suggest the fabrication of similar structures in wide-band gap semiconductor systems, such as wurtzite III-V nitrides [24] and $Mg_xZn_{7-x}O_7$ [22,25,26]. Recently, other types of nanostructures based on the material systems ZnO and $Mg_xZn_{7-x}O_7$ have also attracted interest. [27, 28, 29, 30,31].

In the present work, the geometry, spectroscopic and electronic characteristics of the ternary semiconductor alloy wurtzite $Mg_xZn_{7-x}O_7$ nanostructures were investigated using an ab initio method based on first-principles calculations of density functional theory (DFT).

2. Theory

In this work, we use an ab initio theoretical approach to simulate the properties and nanostructure of $Mg_xZn_{7-x}O_7$ Wurzt-type molecules; this method employs the full electron density functional B3LYP theory (becke, three parameters, Lee-Yang-Parr), the foundation group is 6-311G**. Using B3LYP\6-311G** means correcting the vibration frequency with a scaling factor of 0.965 [32]. All calculations were performed using Gaussian 09 [33] software. The molecular nanoscale confinement of $Mg_xZn_{7-x}O_7$ as a function of concentration was examined in this work. Researchers are attempting to create a restricted number of nanoscale that can be described in the material's wurtzite phase structure (a = b ≠ c) [34- 40], and using the Gaussian 09 software. Figure.1 shows the geometrical structures of the wurtzoid include $MgZn_6O_7$, $Mg_2Zn_5O_7$, $Mg_3Zn_4O_7$, $Mg_4Zn_3O_7$, $Mg_5Zn_2O_7$, and Mg_6ZnO_7were done by using Gaussian 05.

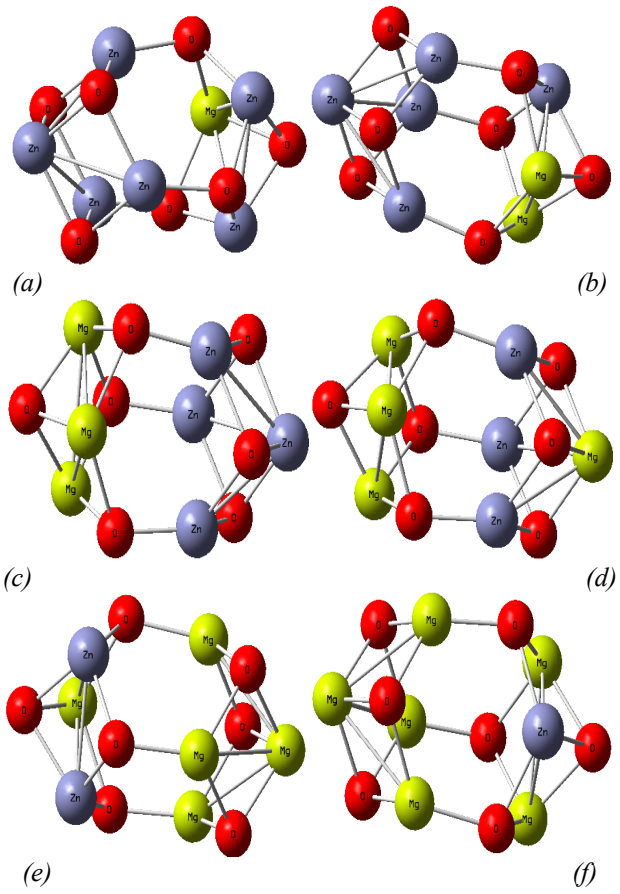

Fig. 1. Geometrical optimization structure MgZnO wurtzoid (a) $MgZn_6O_7$ (b) $Mg_2Zn_5O_7$, (c) $Mg_3Zn_4O_7$, (d) $Mg_4Zn_3O_7$, (e) $Mg_5Zn_2O_7$, (f) Mg_6ZnO_7.

3. Results and discussion

3.1. Electronic properties

3.1.1. Energy Gap

The energy band gap divides metals into conductors, insulators, and semiconductors. The energy range gap is generally associated with the minimum energy needed to transfer the electron from the Valance band (VB) or HOMO (the highest occupied molecular orbital,) to the Conduction band (CB) or LOMO (the lowest unoccupied molecular orbital,). The conduction band is the outermost energy band where free electrons are located, and below it is the valence band. The energy gap of semiconductors ranges from 0.1 eV to 4 eV. [41].

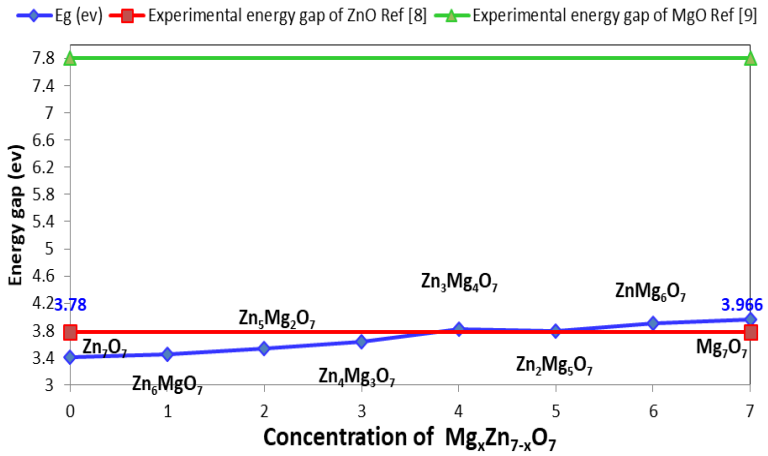

Fig. 2. The band gap of $Mg_XZn_{7-X}O_7$ as a function of Mg concentration and compared with the experimental values.

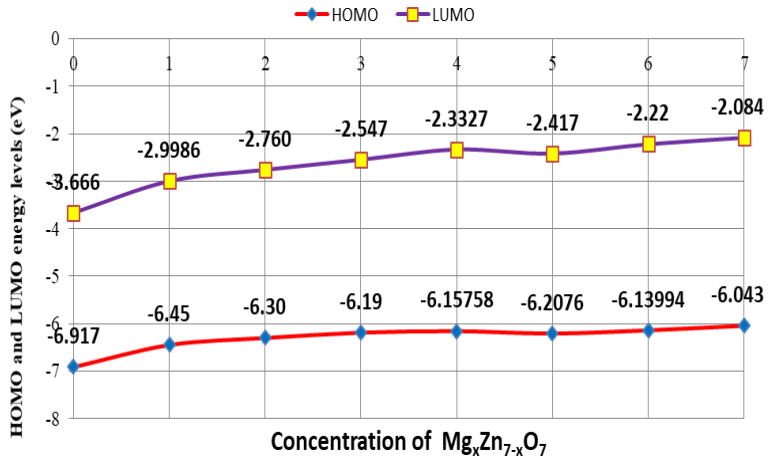

Fig. 3. The HOMO and LUMO of $Mg_XZn_{7-X}O_7$ as a function of Mg concentration.

Figure 2 shows the band gap of $Mg_XZn_{7-X}O_7$ as a function of Mg concentration and compared with the experimental values. Figure. 3 shows the HOMO and LUMO of $Mg_XZn_{7-X}O_7$ as a function of Mg concentration. From figure 2 , We can see that the energy gap of MgZnO increasing with increase Mg concentration, then limited between the experimental value of band gap of ZnO (lower bound) and that of MgO (upper bound). This behavior is due to the different surface reactivity of ZnO and MgO. figure 3 shows that differences in HOMO level values are caused by the energy gap between MgO and ZnO. Since O atoms

always gain electronic charge, these Atoms responsible for almost constant value of LUMO level Both ends of Figure 3 (-3.666 eV for ZnO and -2.084 for MgO). Due to Zn and Mg Atoms donate electronic charges to O atoms, and they are responsible for the dramatic changes In HOMO level values (-6.917 eV for ZnO and -6.043 eV for MgO).

In short, since p If there are atoms at both ends of Figure 3, the LUMO level is relatively constant. and because Zn atoms are gradually transformed into Mg atoms with more abrupt HOMO level changes Result Figure 3.

3.2. Density of Bond Length

The distance between the centers of two covalently attached atoms is known as the bond length. The number of bound electrons determines the bond length (bond arrangement). The greater the attractive force between the two atoms and the shorter the bond length, the higher the bond order. In general, the length of a two-atom bond is equal to the sum of its covalent radius.[42]

Figure. 4 represents the density of bond length distribution of $Mg_3Zn_4O_7$ wurtzoids and compares it to experimental values of Zn-O and Mg-O.

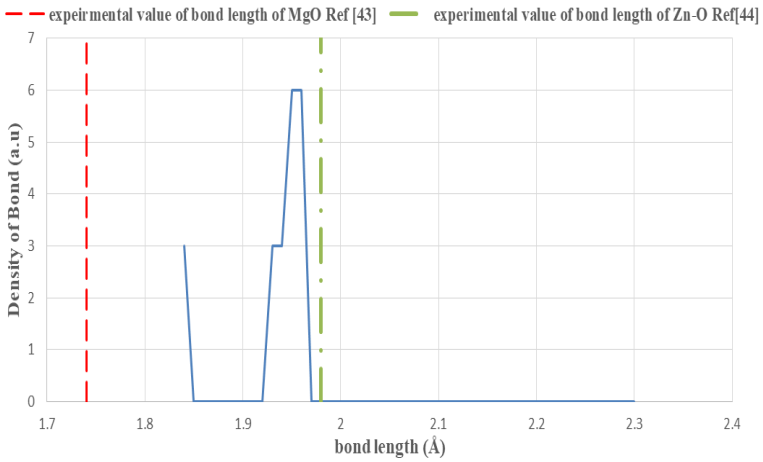

Fig. 4. The density, of bond of $Mg_3Zn_4O_7$ compare with experimental, value of bond lengths of Zn-O and Mg- O.

In figure 4 Mg-O bonds have the longest strong bonds, followed by Zn-O bonds. These bond values agree with the experimental values. Because the calculations are similar to surface calculations, Reconstruction moved many keys away from their perfect length. Experimental values for the above bonds are (1.74 and 1.97, respectively) A□, [43, 44].

3.3. Spectroscopy properties

3.3.1. Raman and IR spectrum

Figure. 5(a,b) shows Raman and IR spectra of MgZnO wurtzoid respectively, as a function of frequencies and compared with the experimental value of longitudinal optical (LO) of MgO and ZnO .

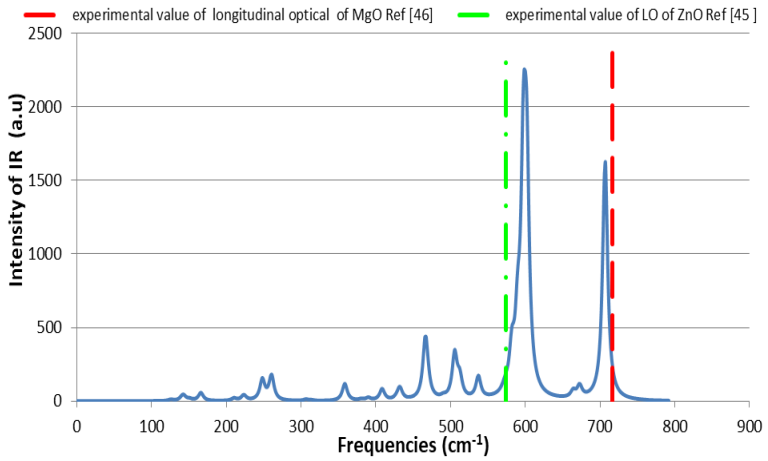

Fig. 5. (a) The IR spectra of $Mg_3Zn_4O_7$ compared to the experimental value of LO of MgO and ZnO wurzite.

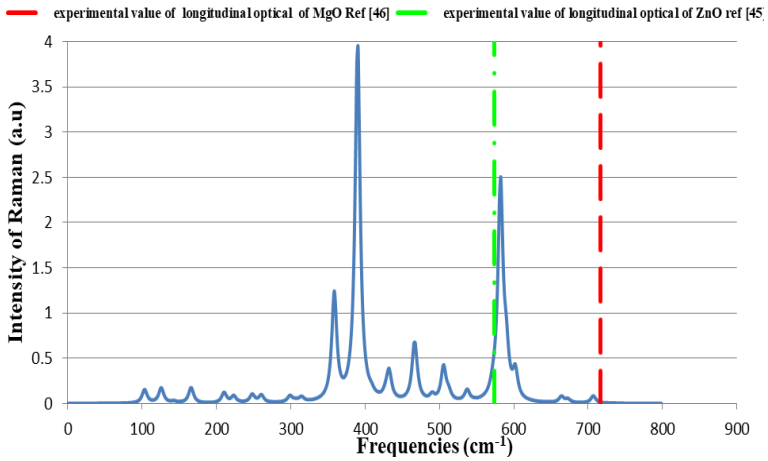

Fig. 5. (b) The Raman spectra of $Mg_3Zn_4O_7$ compared to the experimental value of LO of MgO and ZnO wurzite.

From figure 5 (a), It observed in this figure two regions at (598.4) cm^{-1} and at (707.2) cm^{-1} , the infrared spectrum has very high intensity in these bands. Although figure 5 (b) shows a large number of bands in the two regions of (390.4) cm^{-1} and (582.4) cm^{-1}, the experimental values of the longitudinal optical of MgO and ZnO are (574,717) cm^{-1}, respectively [45,46]. That is, the theoretical value is consistent with the experimental value.

3.3.2. Force constant and Reduce mass

Figure.6(a,b) illustrates the force constant and reduce mass of MgZnO wurtzoid respectively, as a function of frequencies.

$$\upsilon = \frac{1}{2\Pi}\sqrt{\frac{k}{\mu}} \tag{1}$$

where k force constant , μ reduce mass . From equation (1), Frequencies are proportional to constant force but inversely proportional to mass reduction. As a result, the force constant denotes the form of a parabola.[47,48,49]

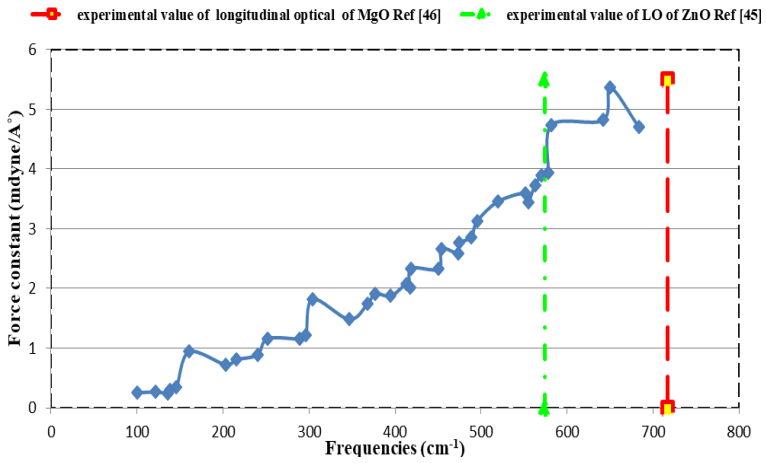

Fig. 6. (a) The force constant of $Mg_3Zn_4O_7$ compared to the experimental value of LO of MgO and ZnO wurzite.

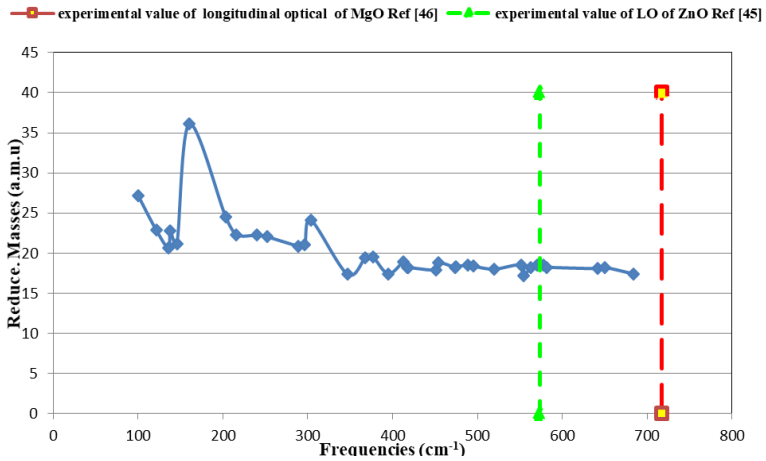

Fig. 6. (b) The reduced masses of $Mg_3Zn_4O_7$ compared to the experimental value of LO of MgO and ZnO wurzite.

In Figure 6 (a,b), the last mode is the longitudinal optical mode (LO). In addition, bare shells have higher frequencies due to the overhanging ligaments on the surface. The effect of dangling keys is that they cause an increase in the force constant.

4. Conclusions

In the present' work, we show that the use of nano-wurtzoids crystals can Provides suitable value patterns for vibrational and electronic properties MgZnO wurtzite material. For example, the two MgZnO composition limits are MgO and ZnO Conversely, because of the presence of d orbitals and other structural and electronic orbitals in heavier Zn atoms Mg and Zn atoms deviate from each other. The discovery of experimental gaps in energy values is closer to practical results for MgO and ZnO wurtzoids, and the energy gap of ternary MgZnO Wurtzoids increases with increasing concentration of Mg. The longitudinal optics of $Mg_xZn_{7-x}O_7$ Wurtzoids blue-shift with increasing concentration of Mg. Therefore, the theoretical results show that

$Mg_xZn_{7-x}O_7$ ternary alloys are potential candidates for optoelectronic materials, especially for UV photon emitters and detectors.

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