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IMPACT OF THE HYDROGENATED ON CHARACTERIZATIONS OF ZnSe WURTZOIDS BASE ON DFT"

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ZnSe chalcogenide material is studied theoretically as wurtziods nanotubes that can be formed from wurtzite structure in case bulk at the stable state by employing DFT and utilizing 3-21G base set after geometrical optimization. In the present investigation, some the electronic and vibrational features of wurtzoids ZnSe are studied for bare(B) or passivated of H –atom (Hp), like energy band, bonds length(b_l) and density states. On the other hand, found that difference between gaps of ZnSe wurtzoids around of bare (3.38 eV) and (4.87)eV of Hp wurtziod due to Affect the hydrogenized on clusters. In addition, the free energy of Gibbs is calculated for ZnSe wurtziod to a limitation which the structures either wurtziod or daimondzoid that have stability at nano-scale.

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Keywords: ZnSe wurtziod, Nanotubes, Nanostructure, DFT

1. Introduction

ZnSe represents binary chalcogenide semiconductor that has gap 2.7eV be a wide and direct and exciton binding energy is 21meV at ambitious conditions[1], also the bandgap of ZnSe is less than others chalcogenide such as ZnO and ZnS[2], but greater than CdS[3]. ZnSe was studied theoretically and experimentally within reason can be used in many devices as windows or lenses, sometimes utilizes as photodetectors, beam expanders, solar cell and there many technological applications for this semiconductor. It has two phases cubic or wurtzite as similar of materials exist in group of chalcogenide. The positions of Zn atom (0, 0, 0)at xyz, while Se atom is located at (1/4, 1/4, 1/4) at cubic structure, respectively[4]. It has absorption be very low in the infrared region as well the highest photosensitivity, also can use ZnSe in visual display and hetero-structures [5]; therefore, ZnSe important to study the electronically and geometrical due to its wide applications. The energy gap of ZnSe that calculated theoretically via the empirical method by Walter et. al.[6], Rachidi1et.al [7] based on (FP-LAPW) method developed in the calculations of first principle study and used the approximations (LDA) and (GGA) to study the properties of cubic ZnSe compounds that have space group F43.

In this work, focused on ZnSe hexagonal (wurtzite) which has point group 6mm and space group P63mc that can build blocks wurtziods of ZnSe to study some merits via first-principle study.

2. Theory

In this paper, most of the properties of ZnSe wurtziod investigated theoretically at ground state of molecules, the calculations performed by using GGA and correlations change available in density functional theory, where error percentage is 0.0015 of bond length while 0.027 for energy, based on DFT takes all electrons in account; therefore, it the best to use this route in the calculations. In beginning, take ZnSe as molecule alone, then start to build the molecule base on variation size of molecules until reaches to ZnSe wurtzoids, all molecules have been calculated by program Gaussian 09 and plot in Gauss view 05, it can see the molecules in Fig.1, the ZnSe divided into three groups wurtziod (Zn_7Se_7), wurtziod 2c($Zn_{13}Se_{13}$) and finally triwurtziod ($Zn_{21}Se_{21}$) without H-atom (Bare) while wurtziod with H-atom ($Zn_7Se_7H_{14}$) as in Fig.1.

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All properties in this work studied theoretical and compare with the results of experimental only for case wurtziod ZnSe like (one nanotube) in cases (bare ,Hp) and compare with ZnSe damaindiozd (cubic), to know affect the H-atom on all features electronically or vibrational and see what happen for molecules at present of H-atom.

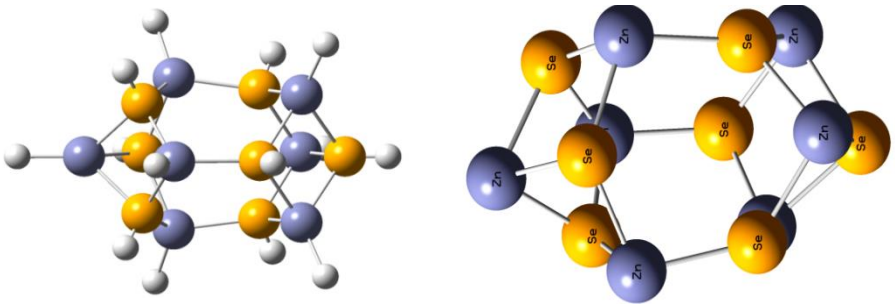

Fig. 1. Structures of wurtzoids, at left with HP ($Zn_7Se_7H_{14}$) and at right Bare (Zn_7Se_7).

3. Results and discussion

Fig. 2 shows a comparison between the density of state of ZnSe wurtziods nanotube $Zn_7Se_7H_{14}$ bare and H-passivation as a function of energy levels, note that energy band of HP wurtziod about 4.87 eV while value of bare is 3.38 eV due to adding H-atom increasing value of energy about the experimental value 2.7 eV, where additional states add into forbidden band of molecule ZnSe; therefore, the band is more broadening than the bare case of ZnSe wurtziod [8].

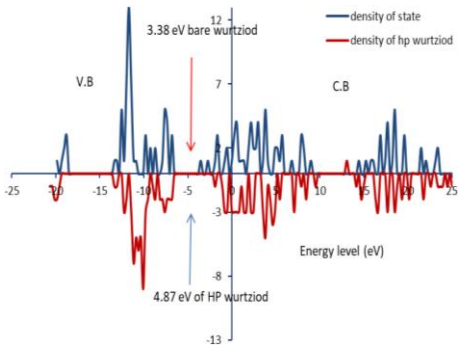

Fig. 2. Comparison energy gaps of wurtziod of $Zn_7Se_7H_{14}$ (B and Hp).

Fig. 3 clarifies bonds length (b_l) of the Zn_7Se_7 wurtzoid determined with Density functional theory. Experimentally, the value of b_l is 2.45 Å for angle Se−Zn−Se[3]while theoretical in this work found that the values of bond Se-H, Se-Se, Zn-Se and Zn-Zn about (1.47, 3.5, 2.45, 3.72)Å for ZnSe Hp wurtzoid, respectively, the bonds were computed theoretical by GGA to solve exchange correlation potential exist in DFT framework depending on 3-21 G , also the bond value of bare Zn-Se and Se-Se is (2.44, 4.08) Å, respectively, the figure is comparing between two states the bare and HP of ZnSe wurtzoid, the negative part in the figure only to represent the comparison. The results can notice increasing in broad bond for HP wurtzoid while be sharp in case bare may belong to effect confinement [2].the bonds of Se-H and Zn-Zn present in case Hp wurtziod but disappear in case bare, i.e. appearance new bonds .

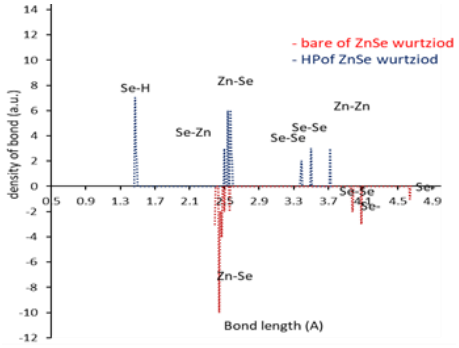

Fig. 3. The theoretical comparison for density of bond of $Zn_7Se_7H_{14}$ wurtziod (Bare and Hp).

Fig. 4 The vibrational features of ZnSe wurtziods that like single nanotube , when connects H- atom with surface of molecules of ZnSe wurtzoid will influence on it is vibrational properties, the frequencies shifted toward high frequencies, IR of ZnSe wurtziods can compare in cases bare and HP , the structures that appear in case IR spectra disappear in Raman. High intensity is 646 and frequencies are 316 cm^{-1} for bare ZnSe Wurtzoids while with H –atom 1975 cm^{-1} and frequency 580 cm^{-1}.

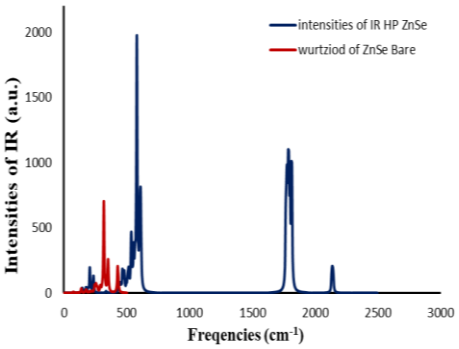

Fig .4 Spectrum IR of wurtziod ZnSe (B,Hp).

Practical findings found that Raman shifts of ZnSe as nanomaterial at 120.96 cm^{-1}, 204.28 cm^{-1} for 2TA, TO and 239.43 cm^{-1} for 1LO, respectively. In the current calculations found that Longitudinal optical (LO) correspond to 270 cm^{-1} for bare while 340cm^{-1} for ZnSe wurtziod Hp as shown in Fig. 5, phonon modes sites of active Raman lines relate to lattice vibrational of materials[9]. The phonon modes LO studies at center Brillouin zone at Γ due to high symmetry of clusters and use GGA approximation that has high accuracy from LDA that neglect the spin of electrons.

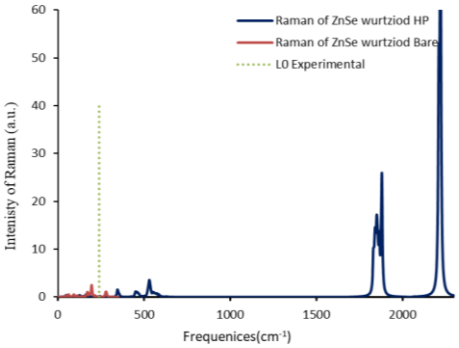

Fig. 5. Spectrum Raman of wurtziod ZnSe (B,Hp).

Fig. 6 compares between reduces masses of ZnSe wurtziods bare and Hp and demonstarte that in case bare the material has higher reduce mass than that passivated of H-atom, the value of LO of ZnSe wurtziods bare is 308cm^{-1} while 239 cm^{-1} for ZnSe Hp, reduces masses of H-atom around 1a.m.u ,the frequneces from 334 cm^{-1} to 1000 cm^{-1} , the frequencies increasing when the mass is light inverse the heavy mass be low frequenecies.

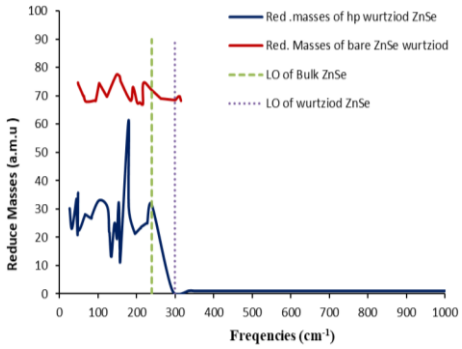

Fig. 6. Comparative reduces masses of wurtziod ZnSe (B, HP) with practical value of LO.

Fig. 7 Explain forces constant of ZnSe wurtziod (B, HP) that made three parabola shapes depending on eq. of $4\boldsymbol{\pi}^2\ \boldsymbol{\nu}^2\boldsymbol{\mu}$ = k, the first parabola for Bare of ZnSe wurtziod, but the second and third represents of ZnSe wurtziod with present of H-atom, the small part of ZnSe while the large for H-atom, as well known that Zn, Se is heavy atoms; therefore, the frequencies will be low, only H-atom passivated be light atom and its frequencies be high at Brilliuon zone and also force constant be high too. The forces constant is (4.01, 1.13 and 2.9) mDyne/Å for ZnSe wurtziod bare and Hp, respectively.

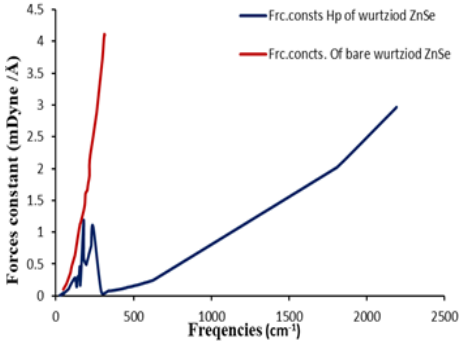

Fig. 7. Comparative forces constant of wurtziod ZnSe (B, Hp) with practical value of LO.

Also comparison the stability of wurtziod (wurtzite) and damaindiozd (cubic) of ZnSe in cause $Zn_7Se_7H_{14}$ at nano-scale. The wurtziod of material be stable if the absolute value of Gibbs free energy(GFE) for $Zn_7Se_7H_{14}$ is 1.22 eV spontaneous (more negative), while $Zn_7Se_7H_{14}$ daimondziod is unstable 1.014 eV be unspontaneous (positive), in order to sure the wurtziod of ZnSe be stable at nano-cale , where most of material be more stable in cause nano-scale [10].

4. Conclusion

ZnSe considers one of the materials that connected weakly with H-atom on its the surface due to Zn is a metal that suffers difficult passivated top surface, as well H- atoms are correlated with strongly between them inversely their connection with metals; therefore, it notices all proprieties will effect with H-atom. The difference between Zn_7Se_7 wurtziod bare and H-passivated become clear in this work. DFT-GGA calculations have been utilized and concluded from GFE that ZnSe wurtziod be spontaneous and stable. The dangling bonds in ZnSe wurtziod Hp impact on its energy gaps.

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