Thermal analysis for stability the nanocrystals ZnSe(diamantane)

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Abstract. The chalcogenide structures are studied at nano scale theoretically. Zinc Selenium is one of these structures studied theoretically by DFT, once as a diamantane (Zn-Se as cubic in solid state) or again diamondoids (Zn-Se:H 14), where similarity in formula but different from wurtziod (Zn-Se) in stoichiometry at nano-limited, the molecules ZnSe diamantane are formed from change size. However both of the spectra and electronic properties of molecules ZnSe diamantane are calculated. In this work, used RB3LYP/3-611 G(p,d) as a base set, it can note that the blue shift of the Raman spectra, the energy gap 2.767 eV for ZnSe diamantane approach to the experimental values, the longitudinal optical of same structure is 208 cm -1, also maximum force and displacement of atoms are investigated. In this research, bond length is 2.46 Å, also investigated the effects on the surfaces of molecules.

Key words: diamantane ZnSe, DFT, Chalcogenide, GFE, ZnSe, II-VI, stability

1-Introduction:
The Nanostructures features in II-VI group at the periodic table became more interesting in nanotechnology field dependent on important of their applications and the modern progress in optoelectronic devices, one of these structures of semiconductors are monochalcogenide Zn that connect with other element X such as (S, Se, O and Te) to form compounds ZnS, ZnSe, ZnO, and so on [1-3].

Most of these compounds more important in technological development where utilized in several applications recently [3] such as high densities in optical memories, devices of the laser or photo detectors, also solar cells etc. currently, most of the researches in the fields of optoelectronics and electronics shown that investigations of electronics and structural features for these appliances have considerable in their development that appear in the new nanotechnologies.
Newly, many researchers studied the properties of compounds above such as electronic or structural by many methods theoretical and employed theoretical calculations in Ab – initio route also used empirical [1-2] some researchers such as Walter and et. al. studied the electronics and band structure characteristics of Zn( Te, Se) by empirical pseudopotential [4], and other Huang and et al [5] that employed LCAO route to computed density of state and band structures of ZnX compounds and group of Karazhanov [2] computed characteristics of the electronic structure by density functional theory (DFT) of ZnX.

Thermal analysis of The Gibbs free energy (GFE) that contain four parameters either be the electronic, or translational, or vibrational and also the rotational, these parameters considered as the freedom degrees of any molecule that impact on the total energy of molecules [6].

There are three cases of GFE: if the GFE case less than 0 (spontaneous reactions or named exergonic) or the GFE case greater than zero (unspontaneous reactions or named endergonic) and finally there is reaction in the equilibrium case if GFE = 0.

To optimize some characteristics of electronics and geometrical or Raman spectrum of ZnSe diamantane(Zn7Se7) as Zinc Blende (cubic) via theoretical calculations that utilized DFT in Gaussian program(09), this simulation required some approximations such as Generalized Gradient Approximation (GGA) which existing in DFT that is included in Ab – initio calculations.

2- Theory:
Theoretically, To study features of ZnSe(Zn7Se7) diamantane that similar to cubic structures in bulk but deferent in number molecules that form the compound where this structures forms at nano-scale and have dangling bonds in end the terminals to ability it to connect with other atoms like H or N … in this study, there are two bonds can connect with the suggested atoms.

DFT applied in this simulation to important it and it has high accuracy to obtain on best results and comparison with the experimental results, and named diamantane comes from diamond carbon and has same shape of it, also diamondoids (Zn7Se7H30) named of molecules that connect with hydrogen. Also Se and Zn considers as heavy atoms that delay during the work in program Gaussian09 may be needed many months to complete it, therefore, in this calculations that focused on diamantane only and neglected the rest like (tetra Zn7Se7H28, hexa Zn7Se7H30, octa Zn7Se7H42 … etc.) that prefix accompany with the diamantane ZnSe with adding H-atom.

In this study used 6-311 G and RB3LYP to represent the molecules in Gauss view 06 and the results of spectrum and all calculations, the previous results used wurztiod of ZnSe as nanotube [7], now in this paper completes the result of diamantane Zn7Se7 (bare) and diamondoids Zn7Se7H30 or take partial diamondoids Zn7Se7H14 similarity in the formula but there different in the structures geometrical with wurztiod (Zn7Se7) that studied previously as shown in figure 1, this molecule formed by various the size molecules. Also used using Gibbs function to know the stability at nano-scale for these structure from thermodynamics calculations.
Figure 1. Shows the geometrical structures of ZnSe (a- diamantane, b- diamondoids).

3-Results
Electronic features of ZnSe diamantane like energy band also the bond length can be noted in two figure 2 and figure 3, found that Eg of this molecules are 2.76 eV approximated to experimental values [8], the band gaps calculated from (HOMO and LUMO) levels that give information about the occupied and unoccupied molecules levels of of ZnSe diamantane, increasing the dangling bonds at surfaces of molecules due to increase energy gaps spontaneously by the adding levels to forbidden gaps [9-10], also all the calculations achieved at temperature 298 °K and pressure 1 atom for molecules at point group C1.

Figure 2. Change the energy levels (HOMO –LUMO) of ZnSe diamantane.

Also bond length of ZnSe molecules as diamantane is 2.46 close to experimental value, where note that board of bond is sharp in this case diamantane of Zn$_7$Se$_7$.
The vibrational properties are studied when imaginary frequency (cm\(^{-1}\)) equal zero: Phonons spectra of ZnSe diamantane that illustrated in figure 1 which come from Raman spectra to study characterizations of ZnSe diamantane, to study longitudinal optical LO for this molecules and comparative with the experimental findings, noted that low intensity for all peaks in Raman reach upper summit of ZnSe to 2.4 a.u., while the other summits be lower, the value of LO of ZnSe is 208 cm\(^{-1}\) less than the experimental.

Raman scattering give more information about the oscillation and dynamics of lattice for any material, also study IR spectra as shows in figure 5. notice that there high intensities of spectra molecules of ZnSe diamantane reach above 700 a.u.

Practically, at the nano-scale found that the findings of Raman shifts ZnSe have values for 2TA (transverse acoustic) and TO (transverse optical) are 120.9 cm\(^{-1}\) and 204.2 cm\(^{-1}\) while 1LO 239.4 cm\(^{-1}\)[11], respectively. Theoretically, phonon mode of LO of ZnSe diamantane is 208 cm\(^{-1}\) less than the practical value.

**Figure 3.** Bond density of ZnSe diamantane.
Figure 4. illustrates Raman shift of ZnSe diamantane (bare).

The positions of phonon modes located at center for Brillouin zone i.e. the clusters have high symmetry at center, also the GGA approximations consider high accuracy used in this calculations instead of LDA approximations where the spin electrons be neglected [7]. The spin of ZnSe molecules singlet and multiplicity =0, also maximum force converged to 0.000053 while maximum displacement not converged 0.027160.

Figure 5: shows IR spectra of ZnSe diamantane(bare).
Gibbs function used in the thermal analysis to know or decide any the structures of ZnSe (diamantane or wurtziod) have stability, after know the absolute values of this function where find in the thermodynamics features of molecules during the computations in program Gaussian 09.

Theoretically, Zn7Se7 diamantane is less stable than wurtziod(Zn7Se7) due to the later has GFE is 1.27 eV spontaneous and (the most negative), inverse the GFE value of wurtziod about 1.004eV be positive and unspontaneous, the substances be stable due to quantum confinement of molecules at nano-limited [9].

4-Conclusion:
The virtual lab used to representation the material theoretically by matrixes system of position the atoms of Zn, Se to obtain on results focused on the geometrical structures of ZnSe diamantane, approaching to the practical values, where Gaussian 09 used for this purpose, therefore, it can study all characterizations of ZnSe diamantane with many methods in theory, DFT considers better than other the ways of theory due to it computed all electrons in structures, also the cage of ZnSe diamantane obtain from size variation of the nano-crystals. The findings have been extracted some properties electronics or spectroscopes for this cage of ZnSe diamantiod or diamantane, also concluded that the stability of the molecules of ZnSe diamantane less stable than wurtziod nano-sturctues from the Gibbs function.

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