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RAMAN SPECTRA AND ELECTRONIC FEATURES FOR NANOTUBES OF ZnSSe WURTZIOD: AB-INITIO

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The ternary alloy ZnS_xSe_{1-x} wurtziod can be designed by simulation of DFT when varies the contents of S and Se atom. Study change band gaps of alloy wurtziod and density state. Density functional theory considers of the best approximations which associated with accuracy to simulate the geometrical, electronic characteristics and lines active of Raman. The clusters $Zn_7S_3Se_4$ wurtziods at nano limited that obtains from wurtzite structure, note that band gaps of alloys decrease with the previous results for ZnS and ZnSe ,also when increase concentrations of Se . Nanotubes of $Zn_7S_3Se_4$ wurtziods can be noted in the geometrical structures, also in this work found that longitudinal optical shifted toward blue. Investigation of Bond lengths with their densities of alloys $Zn_7S_3Se_4$ wurtziods and the comparative with practical values.

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1. Introduction

Most of the semiconductors especially Group II-VI can form alloy either ternary or quaternary that have direct band gap and absorbance coefficients of these alloys is high. These materials can be employed for manufacturing photovoltaic devices with high efficiency. The energy gap of these alloys can encompass range of light spectra based on entire composition [1-2]. ZnSe and ZnS are both of them binary compounds can be combined to form ternary alloy ZnSSe so as to be the optical properties are tunable, specific applications required these tune in energy gap or other optical properties. Lin et. al.[3] synthesized ZnSSe nanorods alloy by solvothermal route and studied some the growth conditions and optical features ,also found that these alloys are exemplary candidates for devices whether optical or electrical.

G. L. Agawane et.al fabricated thin films from alloys of ZnSSe by Chemical bath rout and shown that there are tuning in the energy gaps of all thin films of ZnSSe (3.2-3.12)eV [4],some applications of alloys such as infrared detectors and light emit diode. As well the lattice constants of compounds ZnS and ZnSe for the structures of zinc blend were 5.409 and 5.668 Å, respectively. Se enables from taken the suitable position in the ZnS lattice because of the small mismatch of both lattices for forming quantum dots of ternary alloys

In last years, studies about the topic research wurtziods increased interesting by some authors theoretically, where some materials such as ZnO, ZnS, ZnSe and also alloys such AlGaN are investigated [5-7].

In the recent paper, to complete series wurtziods take alloy of $Zn_7S_3Se_4$ wurtziods which can be simulated by Ab-initio calculations from both the compounds that have stoichiometry Zn_7Se_7 and Zn_7S_7 and calculate the geometrical structures of alloy and characteristics the electronic and the vibrational.

2. Theory

At nano-scale, Construction of the small molecules from wurtzoids have been suggested since 2015 [8], that similar to wurtzite phase at bulk, ZnS_xSe_{1-x} wurtziods can construct from change the sizes of molecules ZnS_xSe_{1-x} as result of change the concentrations of molecules (S,

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Se) where ZnS_xSe_{1-x} wurtziod can represent $Zn_7S_3Se_4$ that obtains of two wurtziods Zn_7S_7 and Zn_7Se_7 in Fig .1 (a,b,c) , after that, can build another shapes from it , like tow nanotubes extended at same axis such as c –axis called wurtziod 2c represent for tow compounds $Zn_{13}S_{13}$ and $Zn_{13}Se_{13}$ while alloys wurtziod 2c that have stoichiometry $Zn_{13}S_7Se_6$ in Fig .1(d), or can contruct three nanotubes closed like bundles meeting at zero at (0,3), these tubes called triwurtziods for both compounds $Zn_{21}S_{21}$, $Zn_{21}Se_{21}$ while one of formulas ternary alloyed $Zn_{21}S_{11}Se_{10}$ in Fig.1 (e) .

The nanotubes of alloys wurtziods have dangling bonds; therefore, it can stack to other atoms such H or N and CO_2 work as sensor. The atoms located at the molecule surfaces have three bonds. The molecules of alloys wurtziods studied by DFT calculations after optimization and using basis sets 3-21 G or 6-311G** of B3LYP route as well as employed GGA that has accuracy in the structure gap of computations, all computations get in Gaussian 09 program.

Having constructed the formula of molecules wurtziod as alloy after varies in x include $Zn_7S_6Se_1$, $Zn_7S_4Se_3$,, $Zn_7S_3Se_4$,, $Zn_7S_2Se_5$, $Zn_7S_1Se_6$ and $Zn_7S_5Se_2$. In this study, we take ternary wurtziod $Zn_7S_3Se_4$ and some the molecules that related with atoms such as H-atom ,in addition to uses GGA nonlocal which be more accuracy than LDA in calculations the properties for any material.

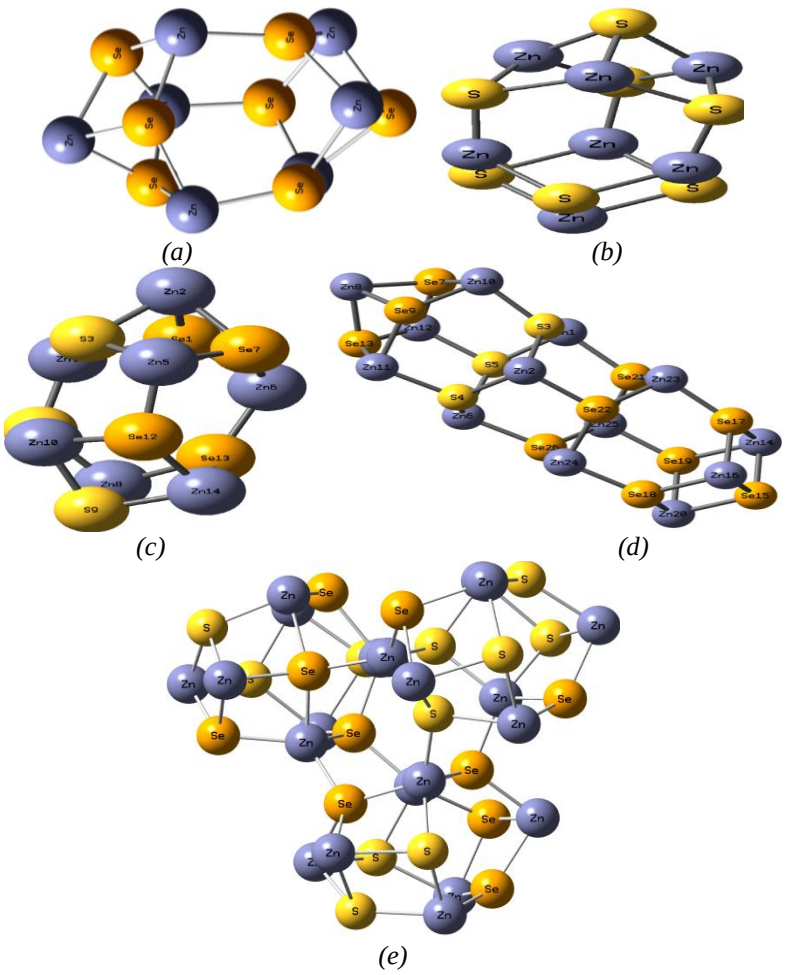

Fig .1. Various sturctures of a) Zn_7Se_7 b) Zn_7S_7 *c)* $Zn_7S_3Se_4$ *d)* $Zn_{13}S_3Se_{10}$ *e)-* $Zn_{21}S_{11}1Se_{10}$ *triwurtziods.*

3. Results and discussion

Fig. 2 shows ZnSSe ternary wurtziods which have point group C1 and the imaginary frequency = 0 at room temp. =298 K and pressure 1 atm. Also to explain the evaluative energy

gaps of ternary ZnS_xSe_{1-x} wurtziods as function of various x found that the band gaps of structures less than the experiment of compounds of ZnS and ZnSe except at x=0 , i.e. at edges approach to the value of band at experimental value. Gaps reduce due to the additional levels that generate at LUMO level that correspond conduct band; these levels decrease the optical gaps since generated tails receives the electrons inside forbidden gap, in addition to calculation the densities of state for some structures alloys such as $Zn_7S_3Se_4$,$Zn_7S_2Se_5$ and two wurtziod Zn_7S_7 and Zn_7Se_7 as in Fig. 3.

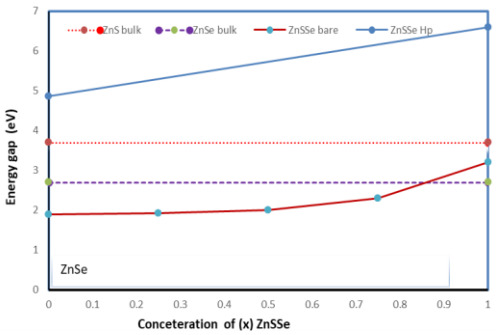

Fig. 2. Energy gaps of ZnS_xSe_{1-x} as a function of Concentrations(x).

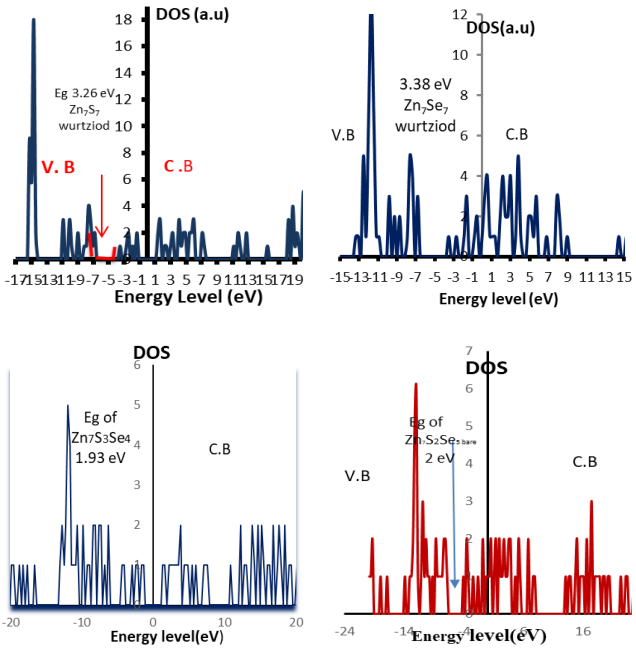

Fig. 3. Band gaps of Zn_7Se_7 , Zn_7S_7 ,$Zn_7S_3Se_4$ and $Zn_7S_2Se_5$ wurtziods (bare).

Note from Fig .4 (a, b, c and d) that Raman lines active for three compositions Zn_7S_7 wurtziod, Zn_7Se_7 wurtziod and alloy of $Zn_7S_3Se_4$ wurtziod when compare with the experimental values each of them 351 cm^{-1},240 cm^{-1} [9-10] for compounds ZnS and ZnSe, respectively. Theoretically, magnitudes the longitudinal modes (LO) and transverse TO of clusters wurtziods represent by 315 cm^{-1}, 194 cm^{-1} 312cm^{-1},respectively.In the other hand, TO of Zn_7S_7, Zn_7Se_7 and $Zn_7S_3Se_4$wurtziod 176 cm^{-1} , 172 cm^{-1} ,182 cm^{-1} respectively, also can indicate that the values of $Zn_7S_3Se_4$wurtziod mediated between two compounds of wurtziods, based on the approximation of DFT and base sets 3-21 G and 6-311G** used in the computations, Raman scattering generated from the oscillated lattices for substances, additionally ,all case obvious us the low intensities for all Raman spectra, also the theoretical values approach to experimental.

The modes of phonon appear when the clusters have high symmetry at its center. The $Zn_7S_3Se_4$wurtziod in this cause be the highest symmetry and be at Γ point in center region of Brillouin zone, i.e. the symmetry will be at center of wurtziods of $Zn_7S_3Se_4$and not in the edges.

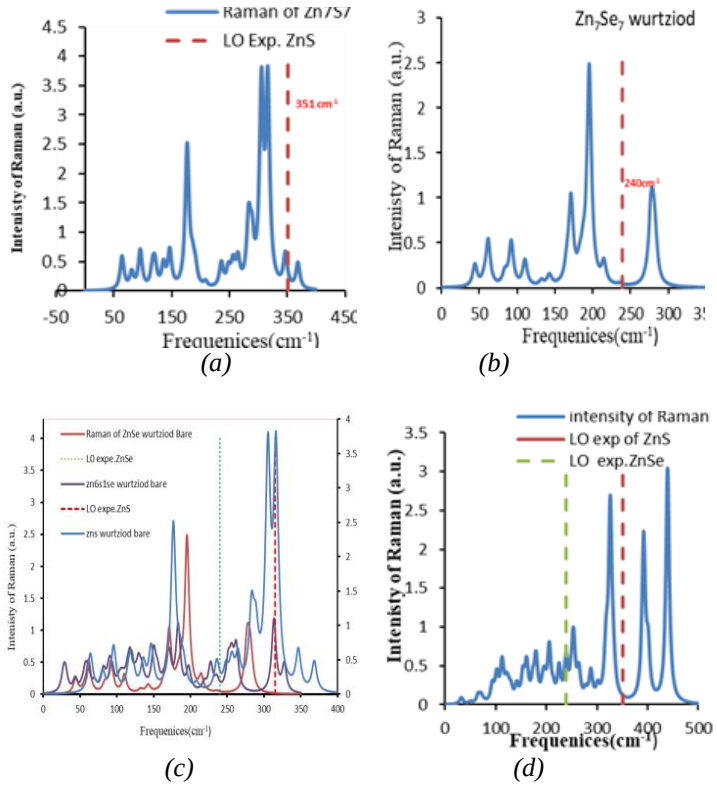

Fig. 4 Raman shift of nanotubes for one of alloys and comparative with a) Zn_7S_7, b) Zn_7Se_7 wurtziods theoretically c) collection all wurtziods d) $Zn_7S_3Se_4$ wurtziods.

In this section, Fig. 5 c comparison for bonds length for $Zn_7S_3Se_4$ wurtziods with Zn_7S_7 and Zn_7Se_7 wurtziods theoretically in addition to mention the values of experimental of these bonds. As well known that the bond associated with lattice constants and impact with it, the theoretical results of the bonds length of Zn-S, Zn-Se, S-Se , 2.38Å, 2.44 Å, 2.27 Å sequentially, while Zn-Zn bond delocalized at 2.56 Å, the bond of S-Se is the shortest form Zn-S ,Zn-Se bonds depending on electron affinity of matter, also note that the bonds of values Zn-S, Zn-Se for alloy $Zn_7S_3Se_4$ wurtziods compatible with previous studies such as [5] and agreement with the theoretical values of $Zn_7S_7$and Zn_7Se_7 wurtziods, but in this study gathered all bonds wurtziod of binary compounds and ternary alloy without any addition on surface the alloy.

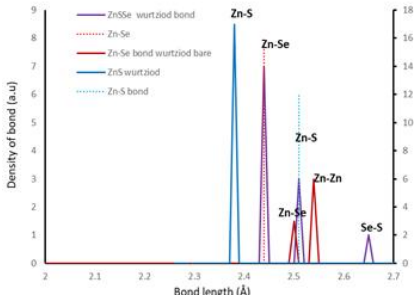

Fig. 5. The bonds length of alloys $Zn_7S_3Se_4$*wurtziods comparative with* Zn_7S_7 *,*Zn_7Se_7 *wurtziods theoretically.*

4. Conclusion

The tunable gaps *of* $Zn_7S_3Se_4$ wurtziods, where notice that their values go between 2.7eV to 3.7eV. The bond length of nano- structures alloys wurtziod may be slightly different or remain same according to compounds, the connection bond type of alloys be tetrahedral. $Zn_7S_3Se_4$ is similar to the structures of Chalcopyrite. The study base on the theoretical models such as Ab-initio to know the properties of $Zn_7S_3Se_4$ nanotubes wurtziod before it is working in the lab. Study sensing the alloys wurtziod of gases such as H- atom found increasing in additional levels after that the gaps become high; the study put away the theoretical comparison for bonds length and energy gaps between $Zn_7S_3Se_4$wurtziod as alloy and miscibility the compositions Zn_7S_7 and Zn_7Se_7 wurtziods which formed the alloys.

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