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Quantum chemical studies on structural stability and electronic properties of GaS nanostructures

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Abstract: The realistic structures of pure, In and Se substituted GaS nanostructures are optimized and simulated using density functional theory with the selection of B3LYP/LanL2DZ basis set. Using vibrational studies and calculated energy, the structural stability of GaS nanostructures are described. Point symmetry group and dipole moment of pure, In and Se substituted GaS nanostructures are also reported. The electronic properties of GaS nanostructures are discussed in terms of ionization potential, electron affinity and HOMO-LUMO gap. The present work provides the information for tailoring GaS nanostructures by substitution of proper impurities. The electronic properties and structural stability of GaS nanostructures can be modified with indium and selenium as impurity which find its application in energy storage and energy conversion devices.

Keywords: gallium sulfide; nanostructure; ionization potential; dipole moment; electron affinity.

Introduction

Metal sulfides are potential functional material which exhibits exceptional optical, electrical, mechanical and magnetic properties. Moreover, the metal sulfides can be used as a heterogeneous catalysis [1, 2] owing to their chemical properties and it also has excellent electrochemical properties leading to applications in energy storage and energy conversion devices [3, 4]. The metal sulfides can be synthesized by many methods namely chemical vapor deposition, solution-based methods and physical vapor deposition. Gallium sulfide (GaS) is one of the important materials among III-VI group semiconductor with two dissimilar stoichiometries such as GaS and Ga_2S_3. In recent days, GaS has drawn considerable attention due to its electrical, highly anisotropic structural, mechanical and optical properties. The direct and indirect band gap of hexagonal GaS is 3.05 and 2.5 eV respectively [5]. It has double layered structure with nonmetal atoms, contains S-Ga-Ga-S sheets with stacking along the c axis [6]. The present research interest is mainly focused on synthesizing different morphologies of GaS, such as nanobelts [7], nanotubes [8], nanowires [9], and nanorods [10]. Medina et al. [11] reported the silylated gallium–sulfur ring systems as single source precursors to hexagonal gallium sulfide (GaS). Isik et al. [12] proposed the interband transitions in gallium sulfide layered single crystals by ellipsometry measurements. Filippo et al. [13] reported the phase and morphological transformations of GaS single crystal surface by thermal treatment. The motivation behind the present work is to tailor the electronic properties and structural stability of GaS nanostructures with the substitution of In and Se atoms and to improve the electronic properties. The density functional theory (DFT) is a promising method to study both electronic properties and structural stability of GaS nanostructures which have been utilized in this work.

Computational Methods

The pure, In and Se substituted GaS nanostructures in the form of nanosheet and nanotube have been optimized and simulated successfully using Gaussian 09 package [14]. The atomic number of gallium and sulfur is thirty one and sixteen respectively. In the present work, different impurities are substituted in intrinsic GaS nanostructures and optimized with the help of Becke's three-parameter hybrid functional (B3LYP) with suitable LanL2DZ basis set [15-17]. The selection of basis set is one of the most important criterions while simulating GaS nanostructures. Therefore, LanL2DZ is a most prominent basis set which is effectively providing the output with pseudo potential approximation [18]. Moreover, it is also much suitable for Hf-Bi, Li-La and H elements. The density of states spectrum (DOS) of GaS nanostructures are obtained using Gauss Sum 3.0 package [19].

Results and Discussion

The main focus of this work is on calculating dipole moment (DM), ionization potential (IP), chemical hardness (CH), chemical potential (CP), electron affinity, HOMO-LUMO gap, calculated energy and vibration studies of GaS nanostructures with the substitution of proper impurities such as indium and selenium.

Figure.1 (a) Structure of pure GaS nanosheet

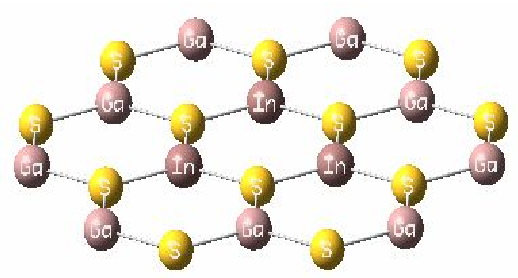


Figure.1 (b) Structure of In substituted GaS nanosheet

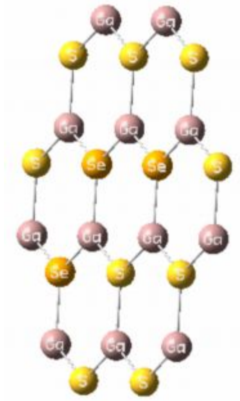


Figure.1 (c) Structure of Se substituted GaS nanosheet

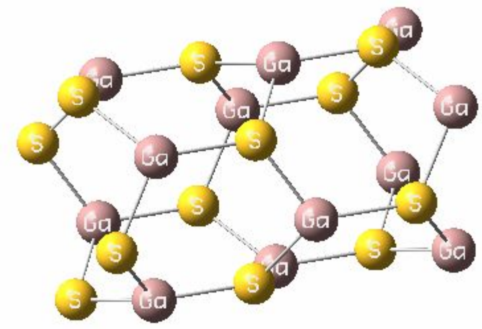


Figure.1 (d) Structure of pure GaS nanotube

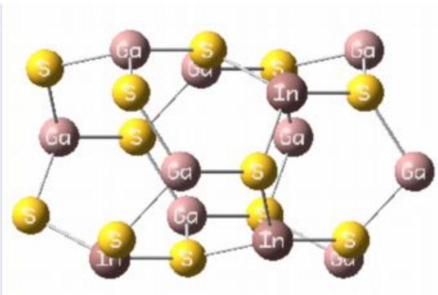


Figure.1 (e) Structure of In substituted GaS nanotube

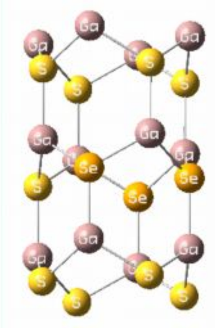


Figure.1 (f) Structure of Se substituted GaS nanotube

Figure 1 (a) – 1(c) represents pure, In and Se substituted GaS nanosheet respectively. The intrinsic GaS nanosheet consists of twelve Ga atoms and twelve S atoms to form sheet like structure. In substituted GaS nanosheet contains twelve S atoms, nine Ga atoms and three Ga atoms are replaced with equivalent three In atoms. Se substituted GaS nanosheet has twelve In atoms, nine S atoms and three S atoms are replaced with three Se atoms. Similarly, Figure 1 (d) – Figure 1 (f) illustrates pure, In and Se substituted GaS nanotube respectively. The intrinsic GaS nanotube consists of twelve Ga atoms and twelve S atoms. The In substituted GaS nanotube has twelve S atoms, nine Ga atoms and three Ga atoms are replaced with three In atoms to form tube like structure. In the case of Se substituted GaS nanotube, it has twelve Ga atoms, nine S atoms and three S atoms are replaced with three Se atoms.

Table. 1 Energy, Point symmetry and Dipole Moment of GaS nanostructures

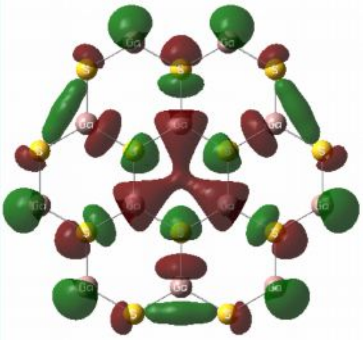
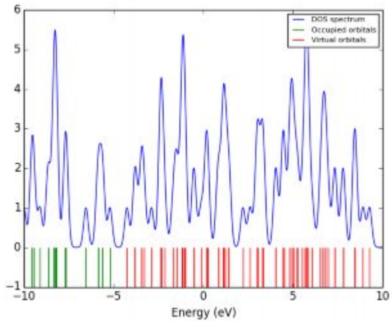
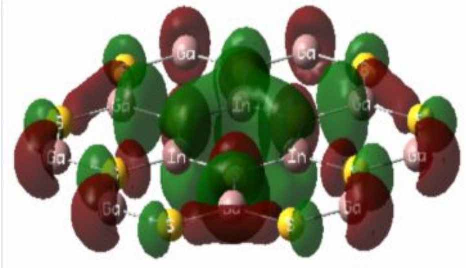
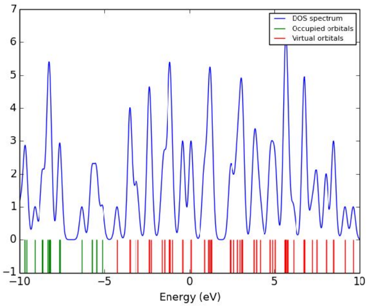
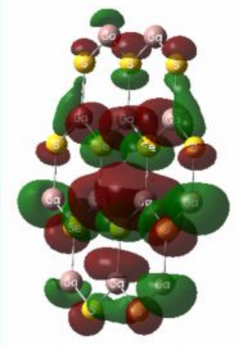
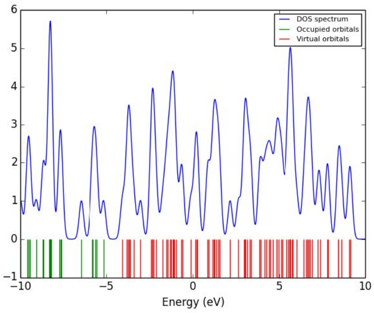
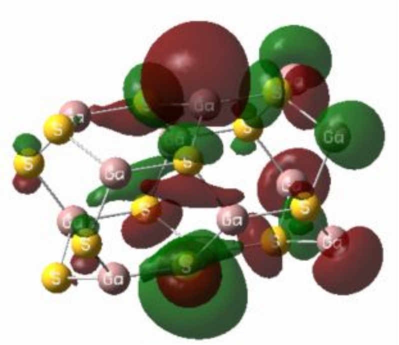
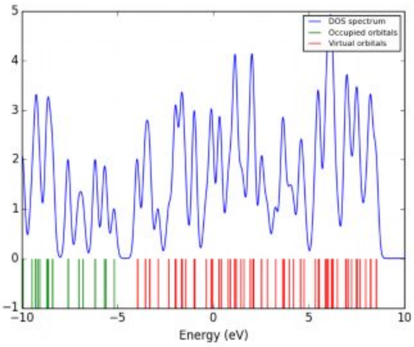
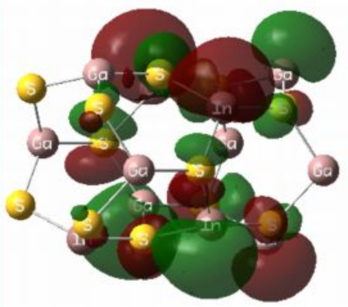
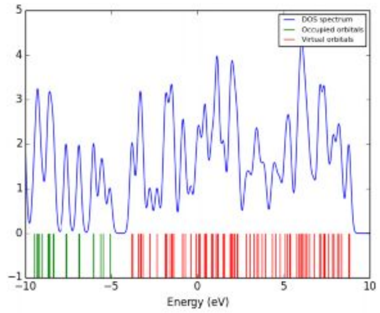
Nanostructures	Energy (Hartrees)	Dipole moment (Debye)	Point Group
Pure GaS nanosheet	-146.63	0.01	C_S
In substituted GaS nanosheet	-146.01	0.01	C_S
Se substituted GaS nanosheet	-143.89	0.49	C_S
Pure GaS nanotube	-146.51	4.59	C_{4V}
In substituted GaS nanotube	-145.87	3.94	C_1
Se substituted GaS nanotube	-143.77	4.14	C_S

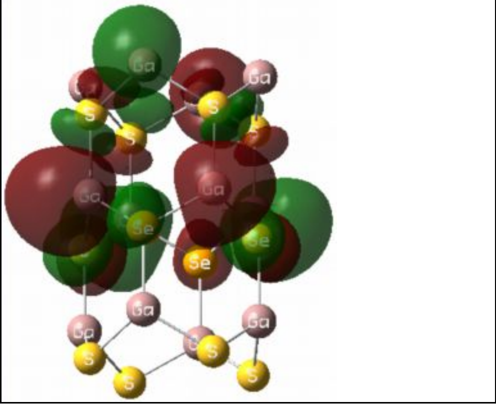
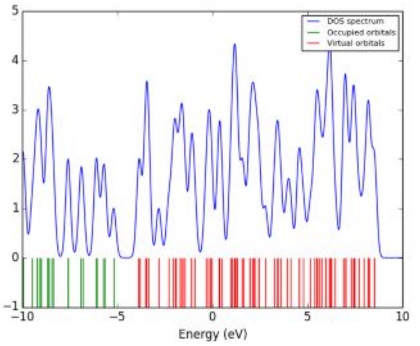
The structural stability of GaS nanostructures can be defined using calculated energy. The dipole moment, calculated energy and point symmetry group of pure, In and Se substituted GaS nanostructures are tabulated in Table 1. The calculated energy of pure, In and Se substituted GaS nanosheet are -146.63, -146.01 and -143.89 Hartrees respectively. Similarly, the corresponding calculated energy value of pure, In and Se substituted GaS nanotube are -146.51, -145.87 and -143.77 Hartrees. Almost same trends are observed in the structural stability of GaS. However, the stability of GaS nanostructure slightly decreases due to substitution of In and Se impurities. Comparatively, pure GaS nanosheet and nanotube have high value of calculated energy. It inferred that pure GaS nanostructures are more stable than impurity substituted GaS nanostructures. The DP values of pure, In and S substituted GaS nanosheets are 0.01, 0.01 and 0.49 Debye respectively. In that order, the DP values of pure, In and Se substituted GaS nanotubes are 4.59, 3.94 and 4.14 Debye. From the observation, pure, In and Se substituted GaS nanosheet have lower DP than GaS nanotube. The low values of DP infer that the charges are distributed evenly in GaS nanosheet than in GaS nanotube. The point symmetry group of pure and In substituted GaS nanotube is C_{4V} and C_1 respectively and C_S point group is observed for remaining nanostructures.

The electronic properties of GaS nanostructures can be discussed by lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) [20-23]. The energy gap value for pure, In and Se substituted GaS nanosheet and nanotube are tabulated in Table 2.

Table. 2 HOMO –LUMO gap and density of states spectrum of GaS nanostructures

Nanostructures	HOMO – LUMO Visualization HOMO LUMO	E_g (eV)	HOMO, LUMO and DOS Spectrum

Pure GaS nanosheet		0.94	
In substituted GaS nanosheet		0.87	
Se substituted GaS nanosheet		1.09	
Pure GaS nanotube		1.21	
In substituted GaS nanotube		1.27	

Se substituted GaS nanotube		1.32	

From the observation of energy gap, slight variation is noticed in HOMO-LUMO gap owing to substitution of In and Se impurities. The energy gap value for pure, In and Se substituted GaS nanosheet are 0.94, 0.87 and 1.09 eV respectively. Similarly, the energy gap value for pure, In and Se substituted GaS nanotube are 1.21, 1.27 and 1.32 eV. This can be concluded that the conductivity of GaS nanostructure gets reduced owing to substitution of impurities except in the case of In substituted GaS nanosheet in which the conductivity slightly increases. From all the observations, pure GaS nanosheet is dominant among other GaS nanostructure. Since, both structural stability and electronic properties of pure GaS nanosheet structure are observed to be more. Thus, the electron can easily transit from the valence band to the conduction band. Visualization of density of states spectrum (DOS) and visualization of HOMO-LUMO gap are shown in Table 2. GaS nanosheet and nanotube shows semiconducting behavior. The low value of band gap is observed compared to the experimental value which arise due to the selection of LanL2DZ basis set. From the DOS spectrum, the localization of charges is noticed more in LUMO level than in HOMO level. With the substitution of foreign atoms, the density of charges in both HOMO level and LUMO level gets modified. Therefore, the electronic properties of GaS nanostructures can be fine-tuned with the influence of In and Se impurities.

Ionization potential and electron affinity of GaS nanostructures

The electronic properties of GaS nanostructure can also be discussed in terms of electron affinity (EA) and ionization potential (IP) [24, 25]. Figure 2 depicts the ionization potential and electron affinity of GaS nanostructures. Usually the energy required for detaching electron from GaS nanostructure refers IP and the energy variation due to addition of electrons in GaS nanostructure is referred as EA. Almost same trends are observed for both IP and EA as shown in Figure 2.

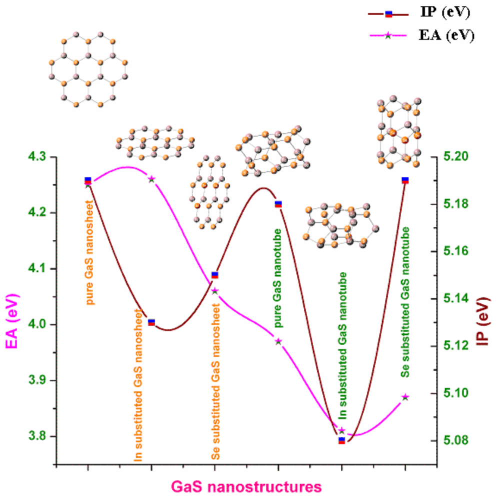


Figure.2 IP and EA of GaS nanostructures

Electron affinity plays a major role in plasma physics and chemical sensors. The electron affinity value of pure, In and Se substituted GaS nanosheet are 4.25, 4.26 and 4.06 eV respectively. Similarly, the EA value of pure, In and Se substituted GaS nanotube are 3.97, 3.81 and 3.87 eV. IP values of GaS nanostructures are observed in the range of 5.08 – 5.19 eV. There is not much variation in IP compared with pure and impurity substituted GaS nanostructures.

Vibrational studies of GaS nanostructures

The structural stability of GaS nanostructures can also be analyzed with vibrational studies. GaS nanostructures are said to be more stable when there is no negative frequency or imaginary frequency. Table 3 indicates the IR intensity and vibrational frequency of GaS nanostructures [26-29]. The pure GaS nanosheet has the vibrational frequency at 269.8 and 412.4 cm^{-1} with corresponding IR intensity of 198.94 and 193.6 km/mole. The In substituted GaS nanosheet has the vibrational frequency at 491.06 and 442.66 cm^{-1} with prominent IR intensity of 201.29 and 109.74 km/mole respectively.

Table. 3 Vibrational Frequency and IR Intensity of GaS nanostructures

GaS nanostructures	Frequency (cm^{-1})		IR intensity (km/mole)	
Pure GaS nanosheet	269.8	412.4	198.94	193.6
In substituted GaS nanosheet	491.06	442.66	201.29	109.74
Se substituted GaS nanosheet	405.67	272.88	140.42	126.8
Pure GaS nanotube	442.33	72.66	201.54	18.73
In substituted GaS nanotube	435	524.97	53.87	32.11
Se substituted GaS nanotube	411.34	438.49	70.28	62.19

Se substituted GaS nanosheet has the vibrational frequency at 405.67 and 272.88 cm^{-1} with respective IR intensities of 140.42 and 126.8 km/mole. Similarly, the pure GaS nanotube has the IR intensity of 201.54 and 18.73 km/mole with the prominent vibrational frequencies at 442.33 and 72.66 cm^{-1} respectively. The IR intensity of In substituted GaS nanotube are observed to be 53.87 and 32.11 km/mole with corresponding vibrational frequencies at 435 and 524.97 cm^{-1}. The prominent vibrational frequency of Se substituted GaS nanotube are 411.34 and 438.49 cm^{-1} and the respective IR intensity are found to be 70.28 and 62.19 km/mole. For all GaS nanostructures, molecular stretching modes are observed. The vibrational spectrum of GaS nanostructures are shown in Figure 3 (a) – 3 (f).

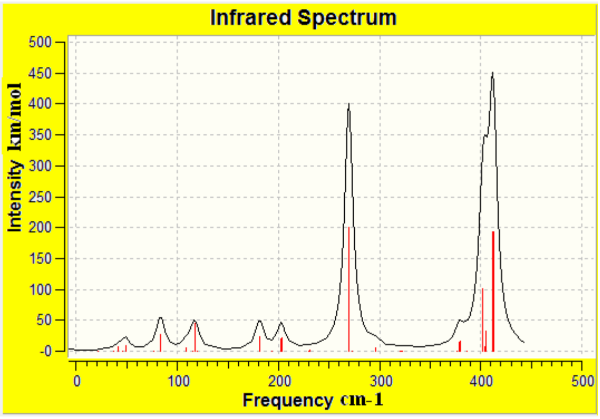


Figure.3 (a) pure GaS nanosheet

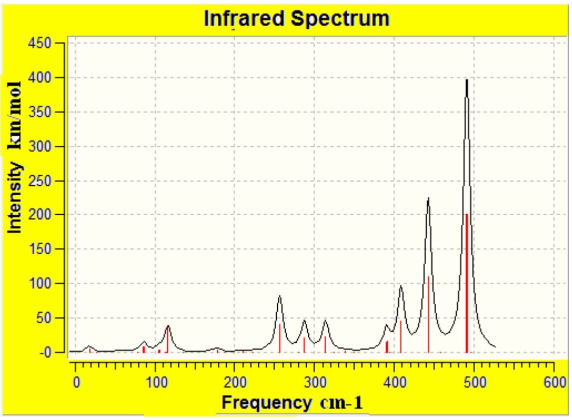


Figure.3 (b) In substituted GaS nanosheet

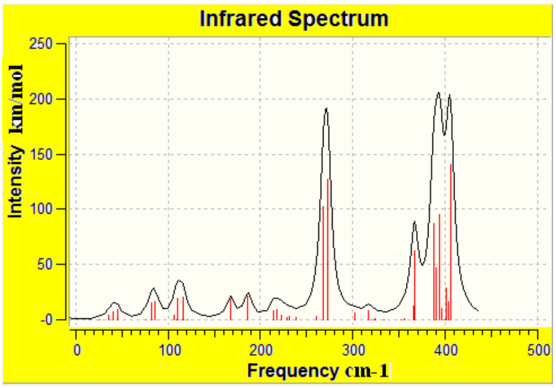


Figure.3 (c) Se substituted GaS nanosheet

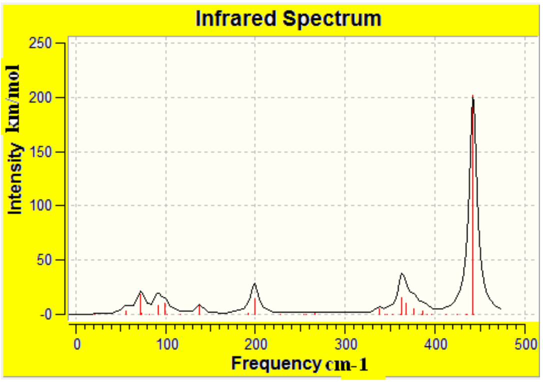


Figure.3 (d) pure GaS nanotube

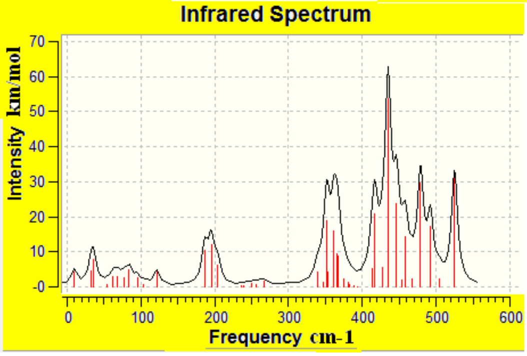


Figure.3 (e) In substituted GaS nanotube

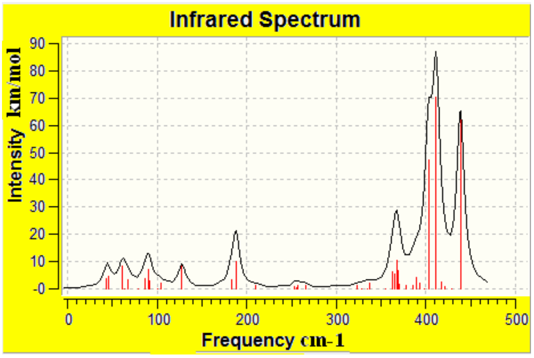


Figure.3 (f) Se substituted GaS nanotube

Conclusion

Using DFT, pure, In and Se substituted GaS nanostructures are successfully optimized and simulated with the help of B3LYP/LanL2DZ basis set. The structural stability of GaS nanostructures are investigated in terms of vibration studies and calculated energy. Point symmetry group and Dipole moment of pure, In and Se substituted GaS nanostructures are also reported. Using electron affinity, ionization potential, HOMO-LUMO gap and DOS spectrum, the electronic properties of GaS nanostructures are studied. In the present work, the electronic properties of GaS nanostructures can be tailored by substitution of In and Se as dopants. Moreover, the structural stability and electronic properties of GaS nanostructures can be fine-tuned with geometry of the structure and by impurity substitution which find its potential applications in energy storage and energy conversion devices.

References

1. Eijsbouts S, Mayo S. W and Fujita K., Unsupported transition metal sulfide catalysts: From fundamentals to industrial application, Appl. Catal., A., 2007, 322,58−66.
2. Chianelli R. R, Siadati M. H, De la Rosa M. P, Berhault G, Wilcoxon J. P, Bearden R and Abrams B. L., Catalytic Properties of Single Layers of Transition Metal Sulfide Catalytic Materials, Catal. Rev. Sci. Eng., 2006, 48(1), 1−41.
3. Lai C. H, Lu M. Y and Chen L. J.J., Metal sulfide nanostructures: synthesis, properties and applications in energy conversion and storage, Mater. Chem., 2012, 22(1),19−30.
4. Cabana J, Monconduit L, Larcher D and Palacin M. R., Beyond Intercalation-Based Li-Ion Batteries: The State of the Art and Challenges of Electrode Materials Reacting Through Conversion Reactions, Adv. Mater., 2010, 22(35), E170−E192.
5. Gasanly N.M, Aydinli A, Özkan H and Kocaba C and scedil., Corrigendum to “Temperature dependence of the first-order Raman scattering in GaS layered crystal, Solid State Commun., 2000,116, 147.
6. Gautam U.K, Vivekchand S.R.C, Govindaraj A, Kulkarni G.U, Selvi N.R, Rao C.N.R., Generation of onions and nanotubes of GaS and GaSe through laser and thermally induced exfoliation, J. Am. Chem. Soc., 2005, 127, 3658.
7. Shen G, Chen D, Chen P.C, Zhou C., Vapor solid growth of onedimensional layer-structured gallium sulfide nanostructures, ACS Nano., 2009, 3, 1115–1120.

8. Hua J.Q, Bando Y, Zhan J.H, Liu Z.W and Golberg D., Uniform and high-quality submicrometer tubes of GaS layered crystals, Applied Physics Letters., 2005, 87, 1–3.
9. Siciliano T, Tepore A, Micocci G, Genga A, Siciliano M and Filippo E., Synthesis and characterization of indium monoselenide (InSe) nanowires, Journal of Materials Science: Materials in Electronics., 2011, 22, 649–653.
10. Sinha G, Panda S.K, Datta A, Chavan P.G, Shinde D.R, More M.A, Joag D.S and Patra A., Controlled growth of well-aligned GaS nanohornlike structures and their field emission properties, ACS Applied Materials and Interfaces., 2011, 3, 2130–2135.
11. Medina I and Fink M.J., Silylated gallium–sulfur ring systems as single source precursors to hexagonal gallium sulfide (GaS), Materials Science and Engineering B., 2005, 116, 375–379.
12. Isika M, Gasanly N.M and Turan R., Interband transitions in gallium sulfide layered single crystals by ellipsometry measurements, Physica B., 2013, 408, 43–45.
13. Filippo E, Siciliano T, Genga A, Micocci G, Siciliano M and Tepore A., Phase and morphological transformations of GaS single crystal surface by thermal treatment, Applied Surface Science., 2012, 261, 454– 457.
14. Frisch M. J et al., Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT., 2009.
15. Chandiramouli R., A DFT study on the structural and electronic properties of Barium Sulfide nanoclusters, Res. J. Chem. Environ., 2013, 17, 64-73.
16. Nagarajan V and Chandiramouli R., Effect on the structural stability and electronic properties of impurity substituted sodium selenide nanostructures–A quantum chemical study, Int.J. ChemTech Res., 2014,6(4), 2240-2246.
17. Nagarajan V and Chandiramouli R., Investigation on the structural stability and electronic properties of InSb nanostructures – A DFT approach, Alexandria Engineering Journal., 2014, 53, 437–444.
18. Srinivasaraghavan R, Chandiramouli R, Jeyaprakash B.G. and Seshadri S., Quantum chemical studies on CdO nanoclusters stability, Spectrochim. Acta, Part A., 2013, 102, 242-249.
19. O'boyle N. M., Tenderholt A. L and Langner K. M., A Library for Package-Independent Computational Chemistry Algorithms, J. Comput. Chem., 2007, 29, 839-845.
20. Ganesan V, Nagarajan V, Saravanakannan V, Chandiramouli R, Quantum chemical insights on tuning structural stability and electronic properties of PdO nanostructures, Int.J. ChemTech Res., 2014, 6(7), 3832-3840.
21. Sriram S, Chandiramouli R, Balamurugan D and A. Thayumanvan., A DFT study on the structural and electronic properties of ZnTe nanoclusters, Eur. Phys. J. Appl. Phys., 2013, 62, 30101.
22. Nagarajan V, Saravanakannan V, Chandiramouli R, Quantum Chemical Insights on Structural and Electronic properties of Anionic, Cationic and Neutral ZrO_2 nanostructures, Int.J. ChemTech Res., 2014, 6(5), 2962-2970.
23. Nagarajan V and Chandiramouli R, Structural Stability and Electronic Properties of Neutral, Anionic and Cationic Cesium Chloride Nanostructures – A DFT Study, Res J Pharm Biol Chem Sci, 2014, 5(1), 365- 379.
24. Nagarajan V and Chandiramouli R., A quantum chemical exploration on structural stability and electronic properties of CdZnO nanostructures, Der Pharma Chemica., 2014, 6 (1), 37-46.
25. Nagarajan V and Chandiramouli R., Quantum Chemical Studies on ZrN Nanostructures, Int.J. ChemTech Res., 2014, 6(1), 21-30.
26. Chandiramouli R, Sriram S and Balamurugan D., Quantum chemical studies on $(ZnO)_n$ /$(NiO)_n$ heterostructured nanoclusters Mol. Phys, 2014, 112, 151-164.
27. Nagarajan V, Chandiramouli R, Sriram S and Gopinath P., Quantum chemical studies on the structural and electronic properties of nickel sulphide and iron sulphide nanoclusters, J Nanostruct Chem., 2014, 4, 87-102.
28. Sriram S, Chandiramouli R and Jeyaprakash B. G., Influence of fluorine substitution on the properties of CdO nanocluster : a DFT approach, Struct Chem., 2014, 25, 389–401.
29. Ganesan V, Nagarajan V, Saravanakannan V, Chandiramouli R, Influence of substitution impurities on electronic properties of CaSe nanostructures – a quantum chemical study, Int.J. ChemTech Res., 2014, 6 (7), 3822-3831.

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