First Principles Study of Cage-like Structures of Sulfur: Structural and Electronic Properties

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Abstract: Naturally, Sulfur is the 10th and 13th most abundant element in the universe and in the earth's crust, respectively. It forms three different allotropes orthorhombic, monoclinic and amorphous but the most stable allotrope is orthorhombic. Theoretical investigation base on density functional theory with SIESTA implementation has been used to determine stability and electronic properties of the cage-like structures of Sn (n=20, 30, 40, 50, 60, 70, 80 and 90). Optimized geometries and electronic characteristics of the cage-like structures are discussed. We have also calculated the Cohesive energies to each structure to check their energetically stabilities. Moreover, HOMO-LUMO gap of the each cluster has been studied to determine electronic properties of the cluster.

Keywords: cage-like structure, cohesive energy, HOMO-LUMO gap, relative stability, thermal stability.

Introduction

Naturally, Sulfur exhibits three different solid allotropic forms i.e. orthorhombic, monoclinic and amorphous. Due to the artificially preparation they can form almost 30 solid allotropes [1]. All the allotropes of sulfur in the bulk form are insulators under the ambient conditions. Only at ultrahigh pressure, phase transition occurs to one dimensional chain, which exhibits metallic behavior [2]. Moreover, below the critical temperature (eg. 10k) with 93 GP pressure it could exhibit superconductor behavior [3]. Theoretically and experimentally, investigation indicates that the sulfur allotropes can transform into two-dimensional layers with the help of host material like molybdenum atoms to create molybdenum disulfide (MoS_2) crystal structure. Layers of S atoms are weakly coupled where layer of Mo is sandwiched between them [4]. In addition, Doping of sulfur atoms onto other materials change electronic properties of the consider materials. Density of state and energy gap of the SiC nanotube change with S-doped [5] and electronic band gaps of graphene change by co-doping with Be and S, and increase form 0 eV to 0.58 eV depending on the doping sites [6]. Adsorption of hydrogen sulfide molecule onto defective graphene change conductivity of the graphene due to the strong interaction of sulfur atoms with the carbon atoms, which are surrounded by vacancies [7] but intrinsic graphene is not efficient material to capture SO_2 [8]. Adsorption of sulfur atom on the surface of Fe(110) with the consideration of three different adsorption sites a top, hollow and bridge sites indicate that the most hollow site is the hollow site [9]. Many materials change their geometric structures and electronic properties with the increasing or decreasing of the number of the constituent atoms. The small Aun clusters have planar structures up to n=6 and structural transition from 2D to 3D take place at the size of seven atoms. In the range of n=10-14 atoms form cage-like structures but around the n=15 transition of the structure occurs to compact near-spherical structure from flat-cage-like structure [10].The pure metal atoms, Aun (n=16-18) hollow cages structures can be stood with one guest atom inside [11] but copper and silver do not form planar and cage like clusters [12]. Although there are many studies exist regarding cage like structures of different element clusters but for sulfur does not. In order to clarify possibility of the cage like structures of sulfur clusters and their properties, which would be helpful to utilize in various electronic applications. This work employs density functional theory (DFT) calculation to determine geometrical stable structures with their energies as well as electronic properties of the Sn (n=20, 30, 40, 50, 60, 70, 80, and 90) clusters.

2 Materials and methods

Density Functional Theory has been employed to find out energetically stable cage-like structures of various sulfur clusters. First principles calculations has been done using SIESTA (Spanish initiative for Electronic Simulations with Thousands of Atoms) simulation package. We have used PBE form of the exchange correlational functional and Generalized Gradient Approximation (GGA) for the calculation of exchange and correlation energies. Conjugate Gradient (CG) method has been used for energy minimization and Double Zeta Polarized basis set for pseudopotential basis set. For optimization of the each structure, we sampled the reciprocal space by a Monkhorst pack grid of $1 \times 1 \times 1$ k point. Mess cut off energy equal to

300 Ry has been used. After the optimization of each structure and minimization of their energies, relaxed coordinates are used to calculate structural and electronic properties of the each structure.

3. **Results and discussion**

Geometrical Structures and their Relative Stability

Molecular structures of the pure S_n (n= 20, 30, 40, 50, 60, 70, 80 and 90) clusters have been studied with the implementation of density functional; theory. After the simulations, we have obtained relaxed atomic coordinates and optimized ground structure of the each cluster. These structures are energetically stable and exhibit different geometrical configuration on their side as shown and illustrated in **Figure 1**. In addition, comparison of stability of the structures with their corresponding energy values are shown in **Table 1**. The S_{80} structure has lowest energy with the minimum value of -317.04 eV/atom. Therefore, it is the most energetically stable structure. Moreover, graph of the energy per atom versus number of Sulfur atoms for cage-like structures is shown in **Figure 2**, which is decreasing and increasing from S_{20} to S_{90} and determines comparatively stability of the structures. Curve of the energy is gradually decreasing from S_{20} to S_{30} and the energies difference is quite small, so these structures are equally stable. It is rapidly decreasing from S_{30} to S_{40}, from S_{40} to S_{50} and rapidly increasing from S_{50} to S_{60} and again rapidly decreasing from S_{70} to S_{80} and their energies differences are comparatively large, therefore, they are not equally stable. It is also increasing gradually from S_{70} to S_{80} and from S_{80} to S_{90} and their energies differences are quite small which means they are equally stable too.

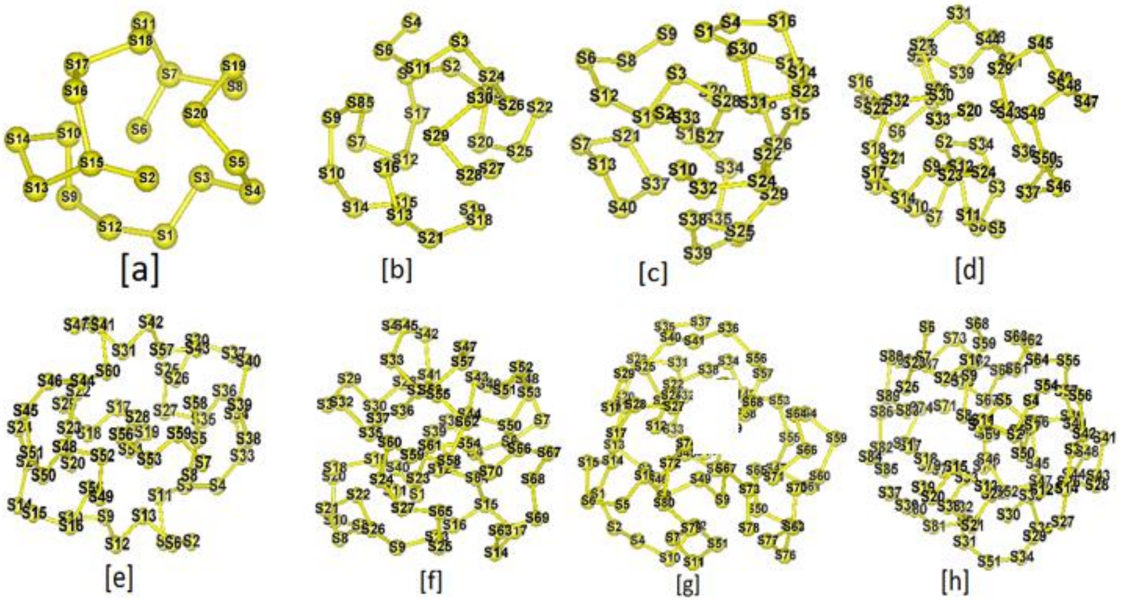


Figure 1 Optimized structures of S_n (n=20, 30, 40, 50, 60, 70, 80, and 90) from [a] to [h], respectively. The figure [a] 18 atoms made closed shape, [b] made open shape, [c] made one pentagon and one heptagon, [d] 13 atoms made closed shape, [e] made open shape, [f] 14 atoms made closed shape with one polyhedron, [g] 13 atoms made closed shape and [h] made one heptagon and one polyhedron

Table 1 *Comparison of energy between different structures*

S. No.	Structure	Total Energy (eV)	Energy (eV/atom)
1	S_{20}	-6338.01	-316.90
2	S_{30}	-9507.08	-316.90
3	S_{40}	-12679.22	-316.98
4	S_{50}	-15850.45	-317.00
5	S_{60}	-19019.77	-316.99
6	S_{70}	-22192.33	-317.03
7	S_{80}	-25362.86	-317.04
8	S_{90}	-28532.20	-317.02

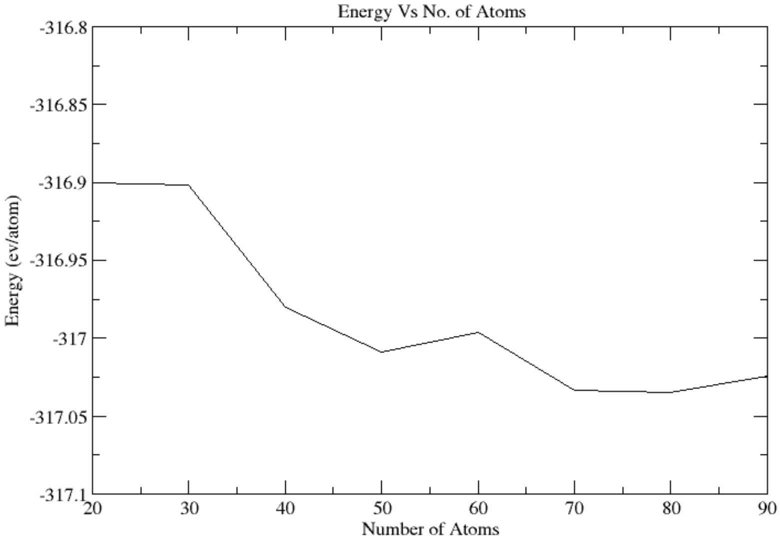


Figure 2 plot of energy in eV/atom Vs number of Sulfur atom

Cohesive Energies

Cohesive energy is the required energy that must be supplied to the solid structure of the atoms to separate its constituents and divide into their individual atoms. It is very important physical property for thermal stability of the solid structure of atoms to calculate strength of the atomic bonds. Cohesive energy of the nanoparticle is different from their bulk counterpart and depends on the size of nanoparticle. It increases with the increasing of the size of nanoparticle and vice versa. Many experimental and theoretical methods have been used to calculate cohesive energy of the different materials. In this work, we have calculated the cohesive energies of each structure:

$$E_C = \frac{E_T - nE_A}{n} \qquad (1)$$

where $E_C$is cohesive energy, $E_T$is total energy of the structure, $E_A$is the single Sulfur atom free energy and n is the number of constituents atoms for each structure. We have found that the corresponding free energy of the single Sulfur atom is (-312.36 eV). We have obtained that the most stable structure is S_{80} with the lowest energy per atom (-4.671). Therefore, to break S80 structure and divide into their constituent atoms requires to the highest energy to supply to the structure. The **Table 2** shows cohesive energy per atom for various cluster structures. The S_{80} structure needs to the highest energy with the amount of (-4.671eV) to break the structure and release one atom. Graph of the cohesive energy per atom versus number of atoms is shown in **Figure 3** and clearly depicts their relations. The cohesive energy difference between the S_{20} and S_{30} structures is quite small, it means they require to same energy for dissociation and for S_{70} and S_{80} is also quite small which require same dissociation energy and show highest stability among the studied structures.

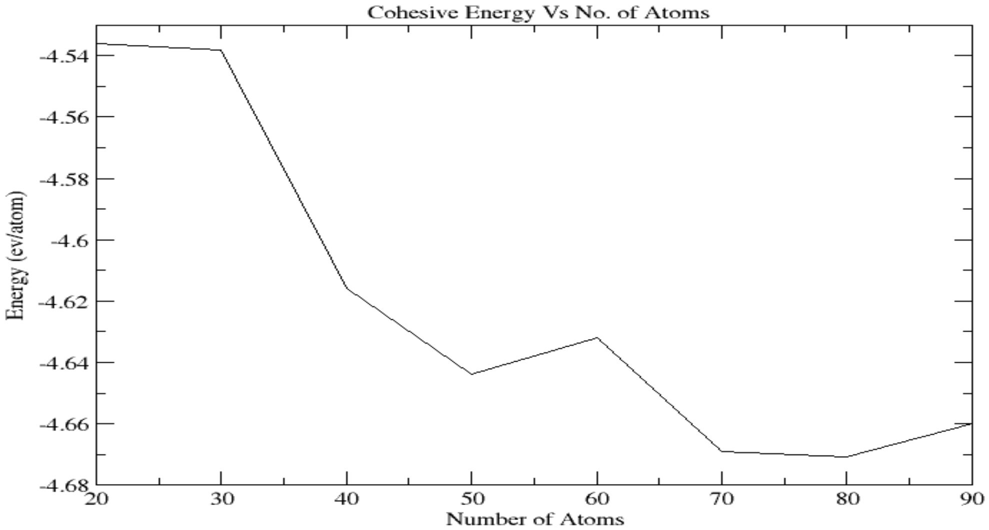


Figure 3 plot of cohesive energy in eV/atom Vs number of Sulfur atom

Electronic Properties of Clusters

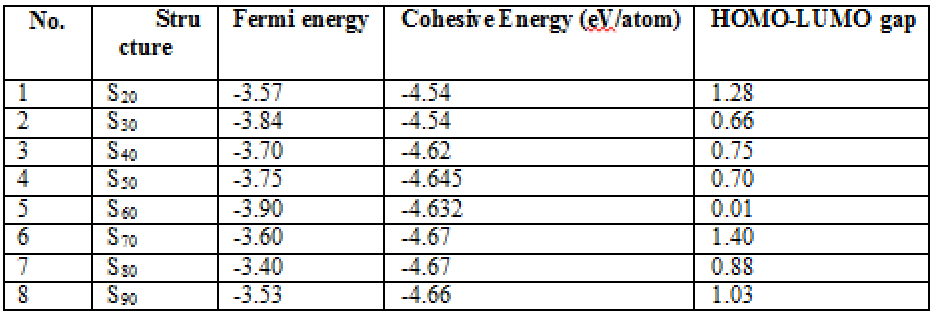
HOMO-LUMO energy gap

For the determination of the electronic stability of the clusters the energy gap between the highest occupied-lowest unoccupied molecular orbital (HOMO-LUMO) is crucial criterion. This energy gap reveals transformation ability of the electron from the highest occupied orbital to the lowest unoccupied orbital [13]. Meanwhile, HOMO-LUMO energy gap can determine electronic nature of the clusters and calculation can be done as follows:

$$E\_g = E\_LUMO - E\_HOMO \qquad (2)$$

The value of HOMO-LUMO energy gaps for pure S_n (n=20, 30, 40, 50, 60, 70, 80 and 90) clusters are listed in **Table 2**. The HOMO-LUMO energy gap for S_{60} is the smallest; with the value of 0.01eV, which is nearly metallic in nature and for S_{70} cluster is the biggest with the value of (1.40 eV). The remaining clusters are semiconductors in nature. Variation of the HOMO-LUMO energy gap versus number of atoms is also plotted in and can be visualized from **Figure 4.**

***Table 2**:. Comparison of Fermi energy, cohesive energy and HOMO-LUMO gap between different structures.*



No.	Structure	Fermi energy	Cohesive Energy (eV/atom)	HOMO-LUMO gap
1	S_{20}	-3.57	-4.54	1.28
2	S_{30}	-3.84	-4.54	0.66
3	S_{40}	-3.70	-4.62	0.75
4	S_{50}	-3.75	-4.645	0.70
5	S_{60}	-3.90	-4.632	0.01
6	S_{70}	-3.60	-4.67	1.40
7	S_{80}	-3.40	-4.67	0.88
8	S_{90}	-3.53	-4.66	1.03

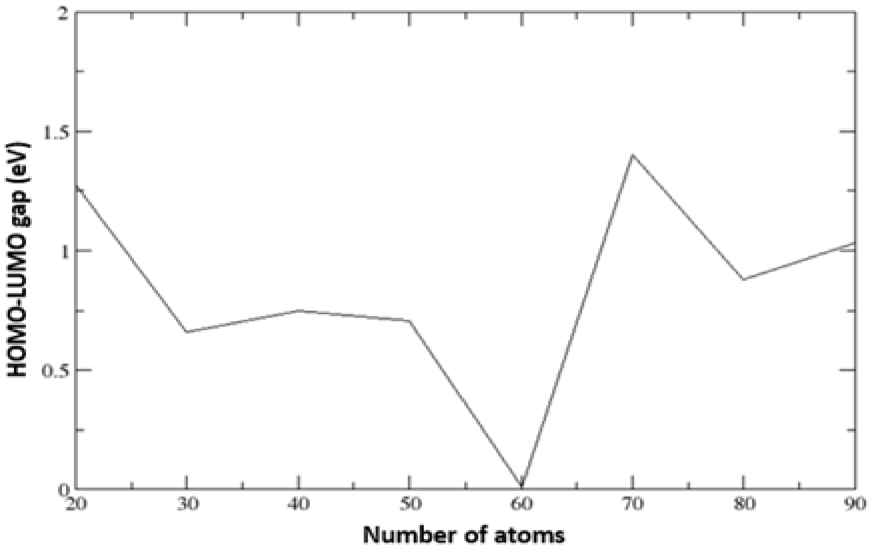


Figure 4 HOMO-LUMO gap Vs No. atoms

4. **Conclusions**

First principle calculation of the Density Functional Theory method was used to analyze and demonstrate physical properties of the various S_n (n=20, 30, 40, 50, 60, 70, 80 and 90) cage-like structures. After the coordinate's optimization, we have obtained free energy of each structure, which is clearly shows, the feasibility of the existence of studied structures. The most energetically stable structure is S_{80} with the free minimum energy value of (-317.04 eV/atom). The S_{20} and S_{30} structures are equally stable, and the structures of S_{80} and S_{90} equally stable too. The cohesive energy of the S_{80} is the highest energy with the amount of 4.671 eV/atom, which shows highest stability of this structure.

Each optimized structure has its own geometrical shape. The structure of S_{40} has one **pentagon** and one heptagon, and the S_{90} structure shows only one heptagon. Using the optimized structures the density of state of each structure is plotted which determines electronic properties of the structure and the HOMO-LUMO gap lies between the 0.01-1.40. From the electronic properties reveal that the S_{60} structure shows nearly metallic nature which has the smallest HOMO-LOMU gap with the value of 0.01eV whereas the S_{70} structure has the highest HOMO-LUMO gap with the amount of 1.40 eV.

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References

[1] R. Steudel and B. Eckert, “Solid **Sulfur Allotropes Sulfur Allotropes,” 2003.**

[2] T. Fujimori *et al.*, “Conducting linear chains of sulphur inside carbon nanotubes,” *Nature communications*, vol. 4, no. 1, pp. 1–8, 2013.

[3] V. V. Struzhkin, R. J. Hemley, H. Mao, and Y. A. Timofeev, “Superconductivity at 10–17 K in compressed sulphur,” *Nature*, vol. 390, no. 6658, pp. 382–384, 1997.

[4] S. Zhu *et al.*, “Metallic and highly conducting two-dimensional atomic arrays of sulfur enabled by molybdenum disulfide nanotemplate,” *npj Computational Materials*, vol. 3, no. 1, pp. 1–8, 2017.

[5] R. S. Singh and A. Solanki, “Modulation of electronic properties of silicon carbide nanotubes via sulphur-doping: an ab initio study,” *Physics Letters A*, vol. 380, no. 11–12, pp. 1201–1204, 2016.

[6] O. Olaniyan *et al.*, “Exploring the stability and electronic structure of beryllium and sulphur co-doped graphene: a first principles study,” *RSC advances*, vol. 6, no. 91, pp. 88392–88402, 2016.

[7] D. Borisova, V. Antonov, and A. Proykova, “Hydrogen sulfide adsorption on a defective graphene,” *International Journal of Quantum Chemistry*, vol. 113, no. 6, pp. 786–791, 2013.

[8] L. Shao *et al.*, “Sulfur dioxide adsorbed on graphene and heteroatom-doped graphene: a first-principles study,” *The European Physical Journal B*, vol. 86, no. 2, pp. 1–5, 2013.

[9] M. J. Spencer, A. Hung, I. K. Snook, and I. Yarovsky, “Sulfur adsorption on Fe (1 1 0): a DFT study,” *Surface science*, vol. 540, no. 2–3, pp. 420–430, 2003.

[10] J. Wang, G. Wang, and J. Zhao, “Density-functional study of Au n (n= 2–2 0) clusters: lowest-energy structures and electronic properties,” *Physical Review B*, vol. 66, no. 3, p. 035418, 2002.

[11] S. Bulusu, X. Li, L.-S. Wang, and X. C. Zeng, “Evidence of hollow golden cages,” *Proceedings of the National Academy of Sciences*, vol. 103, no. 22, pp. 8326–8330, 2006.

[12] E. M. Fernández, J. M. Soler, and L. C. Balbás, “Planar and cagelike structures of gold clusters: Density-functional pseudopotential calculations,” *Physical Review B*, vol. 73, no. 23, p. 235433, 2006.

[13] C.-G. Li, J. Zhang, Y.-Q. Yuan, Y.-N. Tang, B.-Z. Ren, and W.-G. Chen, “Geometries, stabilities and electronic properties of copper and selenium doped copper clusters: Density functional theory study,” *Physica E: Low-dimensional Systems and Nanostructures*, vol. 86, pp. 303–310, 2017.