# SIMULATION OF NANOPOROUS LOW-DENSITY STRUCTURES FROM $ZN_{12}S_{12}$ CLUSTERS

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**Abstract:** *Solid inorganic structures with the same composition but different polymorphisms often have different properties and applications, therefore, synthesizing and predicting new classes of polymorphisms for a given compound are of great significance and have been received considerable attention. In this paper, we propose a bottom-up approach to design nanoporous low-density structures from* $Zn_{12}S_{12}$ *clusters. Depending on the arrangement of the* $Zn_{12}S_{12}$ *clusters, the different polymorphic phases will be obtained. Our results show that the simulated structures are stable, do not collapse in the crystal, and are all semiconductors with wide band gap.*

**Keywords:** *Density functional theory, porous nanostructures, semiconductor materials.*

## I. Introduction

Zinc sulfide (ZnS) is an II-VI semiconductor material, with a band gap of about 3.7eV. It has the advantages of having a relatively large band gap, the ability to withstand strong electric fields, high breakdown voltage, low electronic interference, and can operate at high temperatures with high power. ZnS nanomaterials have many physical and chemical properties which are not found in bulk semiconductors, such as band gap depending on the particle size, stable chemical properties and more applications in engineering than other materials [1]. In particular, when a transition metal ion such as $Eu^{2+}$, $Cu^{2+}$, $Mn^{2+}$, $Co^{2+}$... is doped, they can affect the structure and electronic level transition. Thus, it is possible to control the wide band gap, as well as to control other emission bands in the visible region of ZnS crystals when the impurity concentration and fabrication conditions of the sample are different. Therefore, this type of material has a wide range of applications, for example, in photoelectric devices, phosphor screens, optical sensors, etc.[2]. In its synthetic form, zinc sulfide can be transparent, and can be used as transparent windows to visible light or infrared glass [3].

Since discovery of amazing properties and many applications related to energy and sustainable development, such as catalysis, gas separation, water purification and fuel cells, the field of nanoporous materials has become one of the leading research directions. The main purpose of this research direction is to find materials that possess channels and features which make them become microporous or nanoporous. The most commonly used approach is the bottom-up approach, which starts from a cluster of molecules, by different

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combinations to reach the target structure [4] [5]. In many previous researches [6] [7], we have theoretically simulated several new nanoporous structures of ZnO materials by using the smallest nanoclusters as the basic elements to build up block structures.

Up to now, synthesizing a specific structure has been very important and in most cases remains a challenge. In this article, continuing the bottom-up approach, we will compute simulations based on density functional theory to build up some of nanoporous structures starting from the $Zn_{12}S_{12}$ molecular cluster. Then, we will also discuss the characteristic properties of those nanoporous structures.

## 2. Research Methods

### *2.1. Structural design method*

In the framework of this paper, there are four polymorphic phases that we conduct to simulate and calculate to study their characteristic properties, denoted as SOD , FAU, LTA, AST[2]. The mentioned nanoporous structures all initiate from the $Zn_{12}S_{12}$ atomic cluster (Figure 1), which consists of atoms with the coordination number is three (different from the case in crystals is four), forms rings of even numbers of atoms - due to the equal roles of Zn and S in tetrahedral symmetry, that is, each Zn(S) atom is connected to three S(Zn) atoms by an ionic bonding. In particular, this cluster of $Zn_{12}S_{12}$ atoms consists of eight six-member rings (so called as 6-MR) and six four-member rings (so called as 4-MR), which obey the isolated tetrahedra rules which means there are two different types of Zn-S bonds in the atomic cluster: shorter in two adjacent ring bonds (4-MR) and longer inside the rings (4-MR).

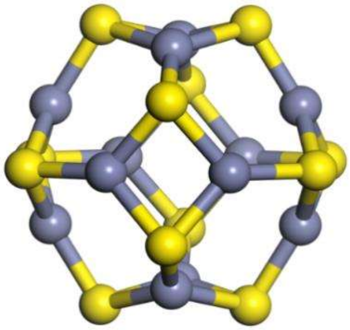

***Figure 1.*** *The relaxed structure of $Zn_{12}S_{12}$ atomic cluster. The yellow balls are S atoms, the grey ones are Zn atoms*

The first SOD polymorphism phase (Figure 2) is created by linking $Zn_{12}S_{12}$ clusters through fourteen tight bonds between all rings of (6-MR) and (4-MR) (We define a tight binding as a linkage that shares a ring bond). When forming the crystalline phase, the number of coordinations of the atoms is four, so that there is no inward contraction since its covalent bonds have been saturated in all directions.

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[2] This acronyms are zeolite framework type code according to the nomenclature of the International Zeolite Association (IZA)

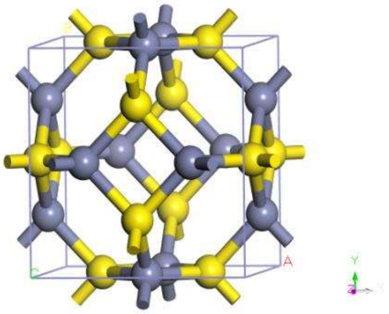

***Figure 2.*** *The SOD polymorphic phase in crystal lattice primitive cell*

Next, the FAU polymorphic phase (Figure 3) is also formed by binding the $Zn_{12}S_{12}$ clusters but differs in the binding method, specifically it consists of four double bonds of the (6-MR). (We define: A double bind is a bond through two bonding rings where the position of atoms do not overlap, close to each other to form bond bridges). Thus, it can be seen that if compared with the SOD polymorphic phase, the linkage between the $Zn_{12}S_{12}$ clusters in the FAU are fewer, less tight (because through the bond bridge rather than tight bond), thanks to this we can see more clearly in the specific bonding energy graph in the detailed calculation (Figure 6).

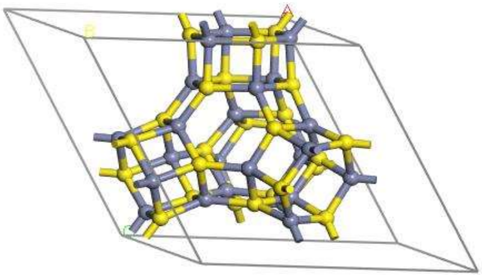

***Figure 3.*** *The FAU polymorphic phase in crystal lattice primitive cell*

For the LTA polymorphic phase (Figure 4), which is created through six double bonds of the (4-MR) in the $Zn_{12}S_{12}$ atomic cluster with six surrounding $Zn_{12}S_{12}$ atomic clusters. Since the bonding behavior between the $Zn_{12}S_{12}$ atomic clusters is different for each crystal phase, the lattice constants of the porous crystalline phases are completely different (Table 1).

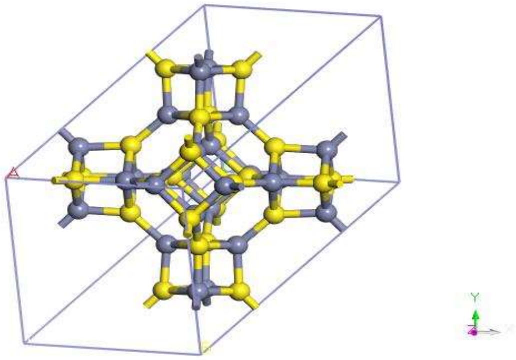

***Figure 4.*** *The LTA polymorphic phase in crystal lattice primitive cell*

For the final AST polymorphic phase (Figure 5), this structure is accompanied by six double bonds of the (4-MR) and eight tight bonds of the (6-MR), distinct from the SOD polymorphic phase with 14 bonds which are all tight bindings even though they come from the same structure. Therefore, the number of atoms in the unit cell is larger (40 versus 12), in addition, the unit cell size (lattice constant), band gap width, specific area of the pore, and the pore volume are also different (Table 1). This shows that SOD and AST are completely different polymorphic phases, although both are derived from the $Zn_{12}S_{12}$ structure, the only difference is in the method of bonding the tetragonal faces.

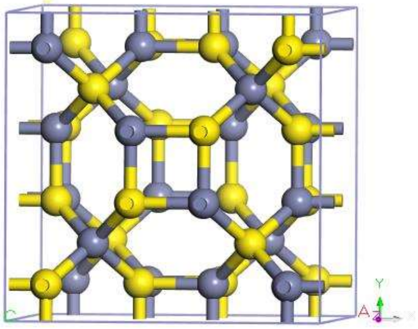

***Figure 5.*** *The LTA  polymorphic phase in crystal lattice primitive cell*

In summary, just from the same basic elements cluster, using the bottom-up approach, with varying the way of association we get different polymorphic phases.

### *2.2. Results and Discussions*

Our calculation results are based on the Density Functional based Tight Binding (DFTB+) method [8, 9] associated with spin polarization and self-consistent charge. This method is based on the expansion of the quadratic approximation of the total energy functional in the Kohn-Sham electronic system depending on the spin of a given reference electronic system and the magnetization density.

#### *2.2.1. Stability of the structure*

Figure 6 shows that the most stable structure is the SOD structure, followed by AST, LTA and finally EMT. This result can be fully explained. Because of all the above structures, SOD is the structure with the most and tightest bonds between $Zn_{12}S_{12}$ clusters (based on 14 tight bindings in all rings), next the AST structure which also has the linkage between $Zn_{12}S_{12}$ clusters through 14 bonds but has both tight and double bonds, the remaining LTA and EMT structures are made up of $Zn_{12}S_{12}$ clusters but only by double bonds.

On the basis of these nonlinear cubic-fitted curves, we can draw some conclusions about the stability of the nanoporous structures. As we had expected, our proposed nanostructures are stable in all cyclic structural systems without collapsing (i.e. breaking) structurally which would lead to existence of their low density nano porous phases.

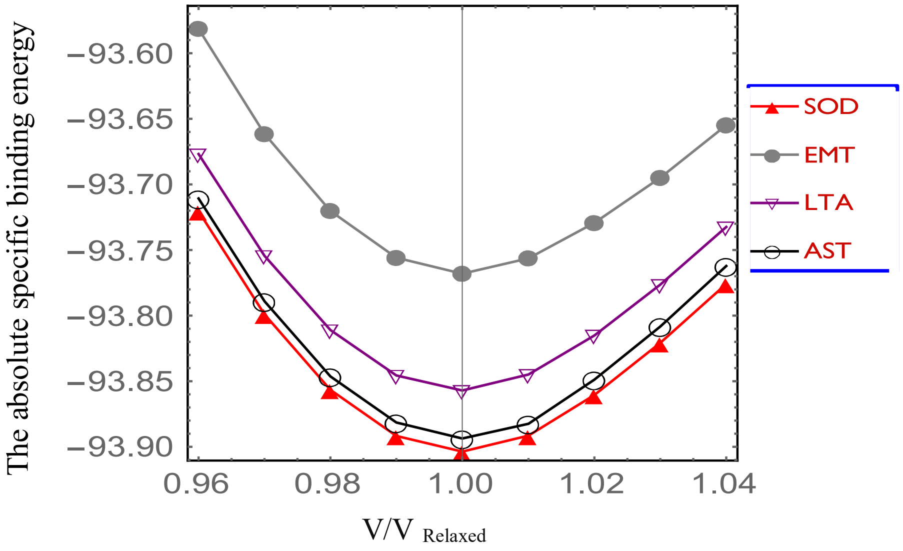

***Figure 6.*** *The dependence of the absolute specific binding energy by the comparative volume*

Figure 7 shows asymmetric differences between the two parabolic branches of the curve in all the structures we have designed. In particular, it is clear that the left branch ($V/V_{relaxed} < 1$) is higher than the right branch, which qualitatively means that stretching will be easier (in terms of energy) than generating compression pressure in all investigated structures.

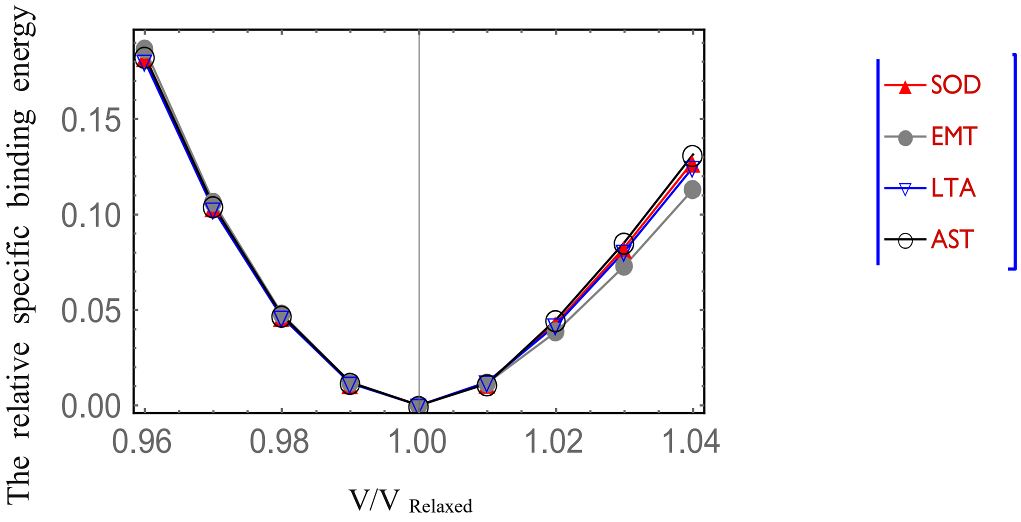

***Figure 7.*** *The dependence of the relative specific binding energy by the comparative volume*

### *2.2.2. Energy band structure*

In this section we study the effect of polymorphism on the electronic energy band structure. It can be seen from the figure 8, each different polymorphic phase has different bandgap and energy band structure.

With the parameterization of the tight binding approximation used in our calculations, the DFTB+ calculation obtains the region widths of the polymorph phases here ranging from 2.9eV to 3.2eV, the largest being the phase LTA polymorphism, and the smallest phase is EMT polymorphism. These wide band gap values are not much different from the band gap of ZnS materials (3.4eV) [11], that is, these polymorphic phases still retain the important and useful properties of bulk ZnS materials.

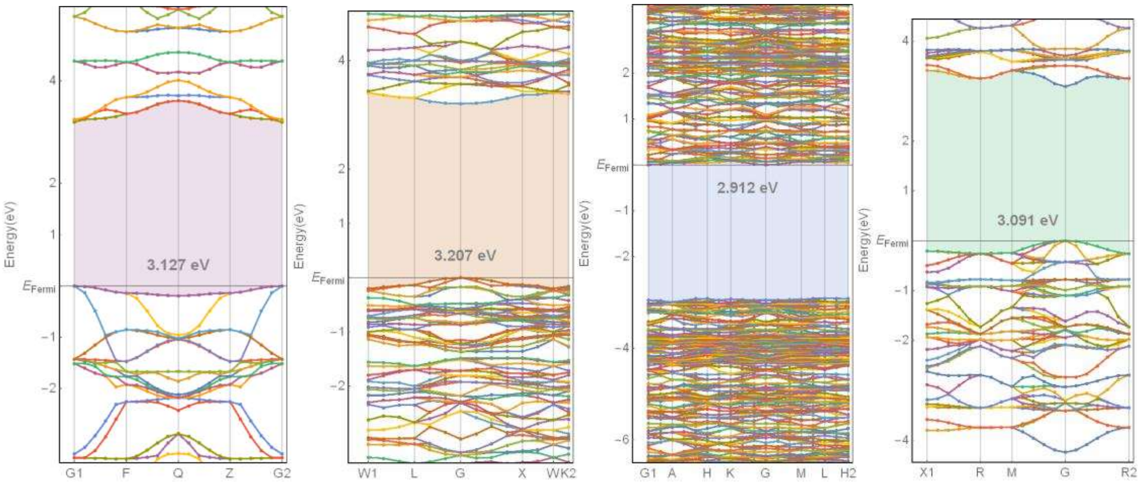

***Figure 8.*** *From left to right is the band structure of SOD, LTA, EMT, AST phases*

### *2.2.3. Structural parameters*

***Table 1.*** *Summary table of structural parameters of ZnS nanoporous phases*

| Structure | SOD | FAU | LTA | AST |
|---|---|---|---|---|
| Mass density (gcm$^{-3}$) | 4.48 | 3.18 | 3.65 | 4.19 |
| Volume /at (Å$^3$/at) | 14.38 | 20.21 | 17.82 | 15.53 |
| Particle density (10$^{23}$cm$^{-3}$) | 12.56 | 48.24 | 48.42 | 40.43 |
| Coordination number | 4 | 4 | 4 | 4 |
| Crystal structure | Cub | Cub | FCC | Cub |
| Unit cell (atoms) | 12 | 48 | 48 | 40 |
| Lattice constant (*a-c*) (Å) | 6.70 | 13.36 | 12.82 | 10.20 |
| Average bond (Å) | 2.027 | 2.040 | 2.032 | 2.031 |
| Average angle Zn-S-Zn | 120 | 110.4 | 121.09 | 125.62 |
| Average angle S-Zn-S | 120 | 110.2 | 118.82 | 124.91 |
| Band gap (eV) | 3.127 | 3.000 | 3.207 | 3.091 |
| Surface area (Å$^2$) | 120.03 | 533.57 | 546.31 | 407.69 |
| Pore volume (Å$^3$) | 94.44 | 865.97 | 674.0 | 351.2 |

As the results show in table 1, in all polymorphic phases-infinite three-dimensional cyclic crystal structures assembled from a series of independent $Zn_{12}S_{12}$ clusters having coordination numbers for all phases are quaternary, that is, each S(Zn) atom has four closest Zn(S) atoms to form a modified hybrid sp3 bond in almost all phases. That is, these polymorphic phases still retain important properties of ZnS materials such as: being a wide band gap semiconductor, piezoelectric, and having optical transparency to visible light. Although produced by the same clusters of $Zn_{12}S_{12}$ molecules, the results in table 1 show that each structure depending on how the different $Zn_{12}S_{12}$ clusters are linked gives us structures with completely different characteristics. Evidence for this is that the mass density, specific volume, particle density, lattice constant, mean bond length, mean bond angle, band gap width of porous structures are completely different. Naturally, each of these porous structures has completely different optical and mechanical properties. Here we also conduct a detailed assessment of the properties of hollow cages or porous walls through quantities such as the pore volume as well as the specific surface area of the energy-optimized or restored pore lattices of the unit cell or base cell of phases, the results allow an assessment of the porosity level of these polymorph phases to a certain extent. The results in table 1 show that in the designed structures, the SOD structure is the least porous and the EMT structure is the most porous. In addition, the results of the graphs in the figure 6 also indicate that the desgned porous nanostructures can exist sustainably.

## 3. Conclusion

Our study shows that the simulated polymorphic phases are stable, not collapsing in the crystal. It can be believed that the nanoporous phases produced by assembling clusters of atoms will become an attractive target for the synthesis of nanoporous polymorphic phases. The same comes from the $Zn_{12}S_{12}$ molecular cluster, but in different binding methods, it will give the nanoporous polymorphic phases with different band gap, surface area, pore volume, etc. This is an important factor in the experimental orientation as well as the practical application of porous nanostructures.

As a result, these new nanoporous phases, if synthesized, will be one of the most promising candidates to replace expensive, mechanically fragile or brittle materials. These porous structures can be used in molecular filtration, many applications in the field of catalysis, purification, oil refining technology etc. Due to their porosity and hollow cage structure, these structures can contain, purge, i.e. pass through or prevent and/or retain within its lumen atoms/molecules corresponding in size to pores or styroform.

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