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A STUDY ON THEORETICAL PREDICTION OF NANOPOROUS STRUCTURES FROM ZnS SEMICONDUCTION MATERIALS

Nguyen Thi Thao[1]

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Abstract: *Nanoporous structures have different properties and applications without changing the chemical composition. Therefore, predicting and synthesizing new nanoporous polymorphs of ZnS has a practical significance and has become one of the strong research directions. In this article, we perform a study based on the DFTB+ method to theoretically predict a series of new nanoporous structures of ZnS. These structures are created from the basic building blocks* $(ZnS)_k$ *(k = 9, 12, 16), they are clusters of molecules with high symmetry. Our results also indicate that all the nanoporous structures are predicted to be completely different mechanical and electrical properties. That proves it is possible to control the mechanical and electrical properties of materials through the configuration of the structure. The characteristic parameters of the ZnS nanoporous structures are examined in detail*

Keywords: *Nanoporous structures; density functional theory; semiconductor materials.*

1. Introduction

Since the finding of excellent properties and many applications related to energy and sustainable development, for example gas separation, catalysis, fuel cells and water purification, the field of nanoporous materials has become one of the strong research directions. The main problem of this research direction is to find materials possessing features that make them become nanoporous or microporous [1].

Nano materials in general and zinc sulfide (ZnS) in particular have many physical and chemical properties that bulk semiconductors do not have such as: band gap depending on particle size, stable chemical properties and more applications in engineering than other materials [2]. ZnS is an II-VI semiconductor material, with a band gap of about 3.7eV, the advantage associated with a relatively large band gap is its ability to withstand strong electric fields, high breakdown voltage, and low electronic interference, and can work at high temperature with a high capacity [3]. This ZnS material has a wide range of applications, such as: photoelectric devices, phosphor displays, and optical sensors, etc. In its synthetic form, zinc sulfide can be transparent and can be used as transparent windows to visible light or infrared glass.

Currently, synthesizing a specific ZnS nanoporous structure is very important and in most cases remains a challenge. The most used approach to design nanoporous structures is the bottom-up approach. This approach involves a cluster of molecules, by

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[1] Faculty of Natural Sciences, Hong Duc University; Email: nguyenthithaotn@hdu.edu.vn

different combinations to reach the purpose structure [4, 5]. In previous studies [6, 7], theoretically, we have also simulated some new nanoporous structures of ZnO materials by using the smallest nanoclusters as basic building elements to build a block structure. In the study [8], the author simulates some porous polymorphic phases from the $(ZnS)_{12}$ cluster. In this paper, continuing that research direction, we calculate simulations based on density functional theory to build some nanoporous structures starting from the basic building elements $(ZnS)_k$ (k = 9, 12, 16). Here, we also discuss the mechanical, electrical, and characteristic properties of such nanoporous structures.

2. Research Content

2.1. Bottom-up structure prediction approach

In this work, firstly we simulated four structures, which are denoted FAU, $Zn_{16}S_{16}$, CAN, and SAT. Next, we calculated to study their characteristic properties. The mentioned nanoporous structures all begin from $(ZnS)_k$ molecules clusters (k = 9, 12, 16) (Figure 1), which are highly symmetric structures. Molecular clusters consisting of atoms with a coordination number of three (different from the case in crystals of four), forming 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 hybrid bond.

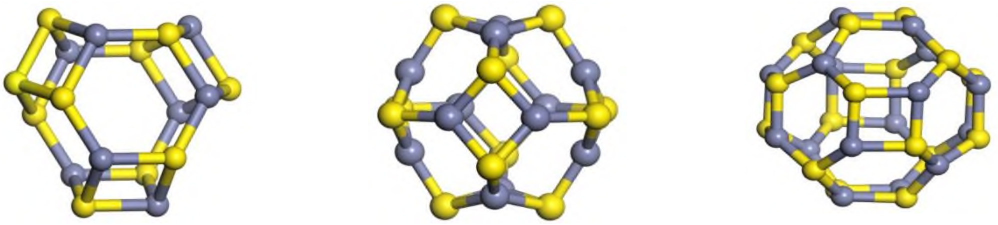

Fig.1. *The relaxed structures, from left to right are* $(ZnS)_9$, $(ZnS)_{12}$, $(ZnS)_{16}$ *molecules clusters. The yellow balls are S atoms, the grey ones are Zn atoms*

The first structure is CAN (Figure 2), which is created by bonding $(ZnS)_9$ clusters (Figure 1a), which is the basic building block consisting of two six-atom rings (referred to as 6-MR) and six four-atom rings (referred to as 4-MR).

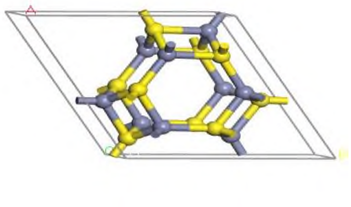

Fig.2. *Simulation image of the CAN lattice cell of ZnS material*

The $(ZnS)_9$ molecular clusters are linked together through two tight bonds (6-MR) and six tight bonds (4-MR), to form an infinitely periodic crystalline polymorphic phase in all three dimensions. The convention tight bond is a link that shares a ring bond. When forming the crystalline phase, the biggest difference of the $(ZnS)_9$ clusters compared to when standing alone is that its coordination will be quaternary for all atoms, so that there is no inward contraction by its covalent bonds are saturated in all directions.

The second structure is SAT polymorphic phase (Figure 3), which is also created by linking the $(ZnS)_9$ clusters like the CAN polymorphic phase, but through a double bond of the ring (6-MR) and six tight bonds of the ring (4- MR). The convention double bond is a link through two bonding rings where the atoms do not overlap, close to each other to form linkage bridges. It is easy to see immediately that compared to the CAN polymorphic phase, SAT is less stable, because the links between the $(ZnS)_9$ clusters in the SAT are less, less tight (because through the linkage bridge, not the tight bonds as of CAN). This can be seen more clearly in the specific binding energy graph in the detailed calculation (Figure 6), where CAN is the structure with the highest specific binding energy (arithmetic value, negative in value). Thus, because the linking method between $(ZnS)_9$ molecules clusters is different for each crystal phase, the lattice constant of the SAT crystalline phase is completely different from that of the CAN crystalline phase (Table 1).

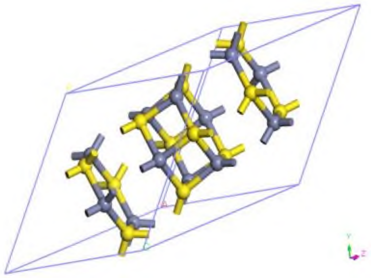

Fig.3. *Simulation image of the SAT lattice cell of ZnS material*

The third structure is FAU (Figure 4), the polymorphic phase again started from the $(ZnS)_{12}$ basic building elements (Figure 1b), which is molecules clusters consisting of eight six-atom rings (6-MR) and six four-atom rings (4-MR). Also from this $(ZnS)_{12}$ cluster, we used it to design four structures [8]. However, in this work, the FAU nanoporous polymorphic phase is completely different from the previous polymorphic phases [8], where the FAU is created through four double bonds of the ring (6-MR) between the basic building elements $(ZnS)_{12}$.

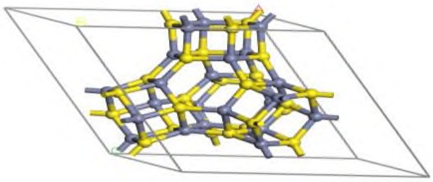

Fig.4. *Simulation image of the FAU lattice cell of ZnS material*

The fourth structure is $Zn_{16}S_{16}$ (Figure 5). This structure is made of $(ZnS)_{16}$ basic building elements (Figure 1c), which is a molecules clusters consisting of twelve six-atom rings (6-MR) and six four-atom rings (4-MR) The $(ZnS)_{16}$ basic building elements is linked, combined through the six double bonds of the rings (4-MR) to created $Zn_{16}S_{16}$ polymorphic phase.

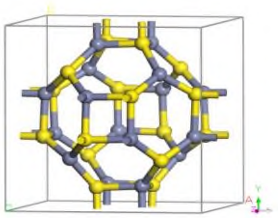

Fig.5. *Simulation image of the $Zn_{16}S_{16}$ lattice cell of ZnS material*

2.2. Results and Discussions

We calculated the characteristic properties of the proposed nanoporous structures based on the Density Functional Tight Binding theory (DFTB+) [9,10]. This method is suitable for studying the electrical and dynamic properties of large microscopic systems or organic molecules such as nanowires or heterostructured semiconductors, etc. The advantage of the DFTB+ method is that the DFTB parameters are only very few, we can select the necessary systems to create the parameters. The DFTB electronic parameters (which are the Hubbard parameters, and the matrix factors $H^{o}_{\mu\nu}$ and $S_{\mu\nu}$) are derived directly from the DFT calculations, performed in general gradient approximation (GGA) and using exchange correlational functionals Perdew, Burke and Ernzerhof (PBE). In our calculations, the parameters and its transformation have been successfully applied in a number of works [6, 7, 8].

2.2.1. Binding energy, phase stability

To compare the stability between the proposed polymorphic phases, we calculate the specific binding energy of each structure by the relative volume (ratio of strained volume and relaxed volume). The curves (Figures 6, 7) show the dependence of the specific binding energy on the relative volume, which are interpolated from the third-order Birch-Murnaghan equation of state [11, 12].

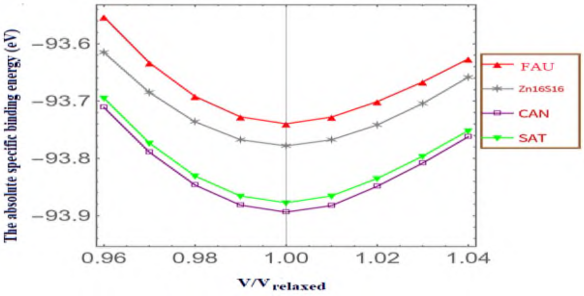

Fig.6. *The dependence of the absolute specific binding energy by the relative volume*

The results in Figure 6 show that the most stable structure is CAN, followed by SAT, $Zn_{16}S_{16}$ and finally FAU. This result is completely consistent and can be explained. Because of all the above structures, The CAN structure is created from $(ZnS)_9$ basic building elements with the most bonds (8 links), which are tight bonds of all rings (4- MR) and (6-MR); the next is the SAT structure, which also has links between $(ZnS)_9$ clusters but through seven links, there are both tight bonds and double bonds; the remaining $Zn_{16}S_{16}$ and FAU structures are created of clusters basic building elements $(ZnS)_{12}$ and $(ZnS)_{16}$ but with fewer bonds and only double bonds. And as we expected, our proposed nanoporous polymorphic phases all stand firmly in the periodic crystalline without collapsing (i.e., structurally breaking), which would lead to the existence of nanoporous phases.

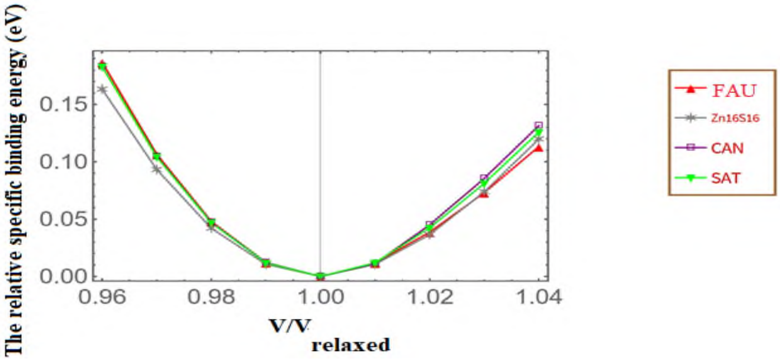

Fig.7. *The dependence of the relative specific binding energy by the relative volume*

The results in Figure 7 show that the obtained graphs are parabolic curves, with asymmetric differences between the two parabolic branches in all the structures we have proposed above. Specifically, we see that the left branch ($V/V_{relaxed} < 1$) is higher than the right branch ($V/V_{relaxed} > 1$), qualitatively this means that stretching (traction) will be easier than generating compression pressure in all proposed structures

2.2.2. Electronic energy band structure

Next, in this section, we study the effect of polymorphism on the electronic energy band structure. As a result, each different polymorphic phase has different band gap and electronic energy band structure (Figure 8).

The DFTB+ calculation results show that the band gap of the polymorphic phases here ranges from 2,616 - 3,292eV, the largest is the CAN polymorphic phase, and the smallest is the SAT polymorphic phase. In which, $Zn_{16}S_{16}$ and SAT structures have a straight band gap (direct); the remaining 2 structures CAN and FAU have an oblique band gap (indirect); and the polymorphic phases that we proposed to study are all semiconductor materials with a wide band gap. In general, our electronic structure study results confirm the fact that nanoporous structures are very sensitive to band gap. This result is very significant for a number of important applications, as this is the basis that allows us to have a band gap microcontroller for low-density materials. Thus, studies on nanoporous phases based on ZnS materials will provide an additional range of properties as well as wider applications for potential functional devices.

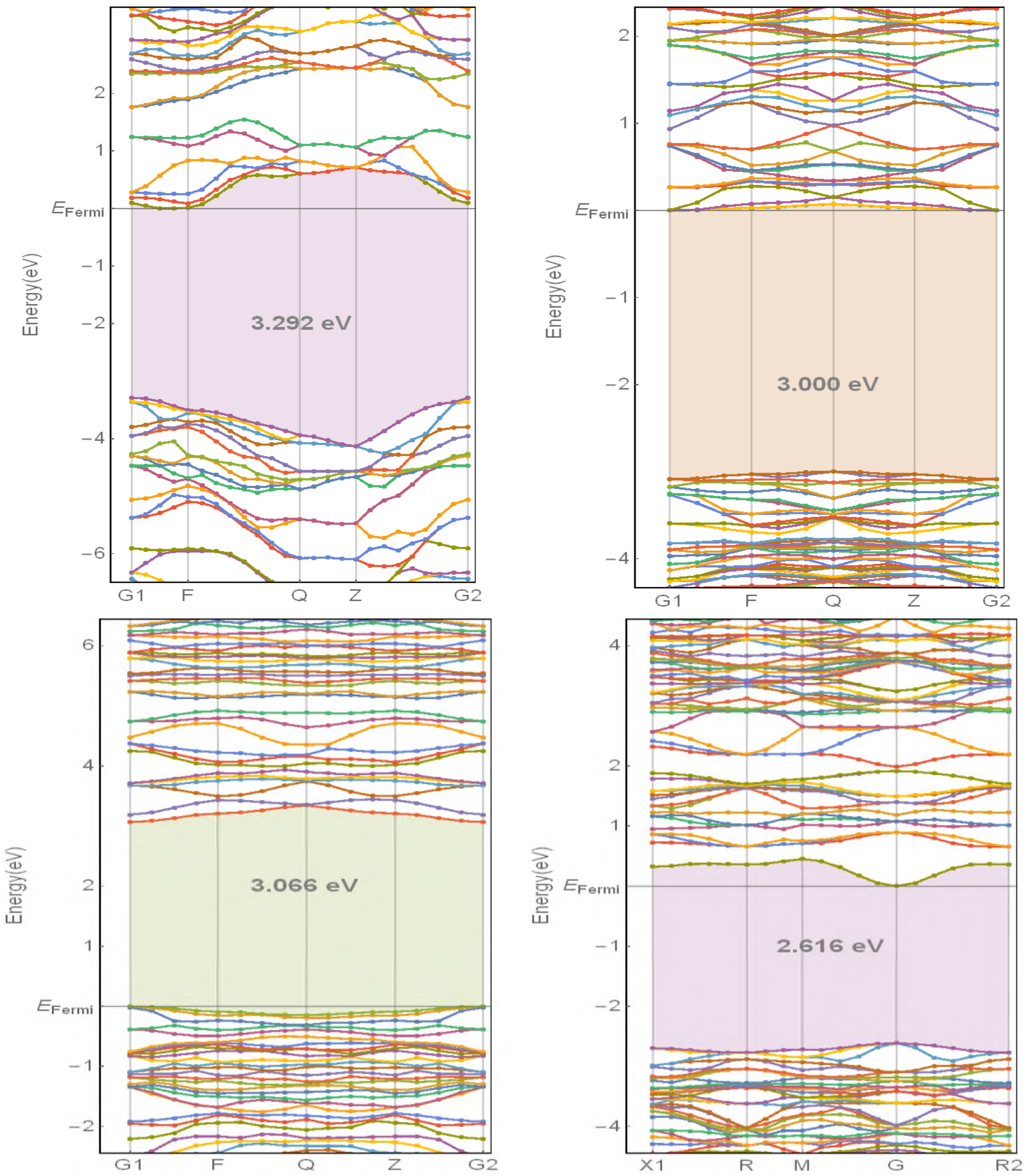

Fig.8. *From left to right, from top to bottom are the band structure of CAN, FAU,* $Zn_{16}S_{16}$ *, SAT phases*

2.2.3. Parameters characteristic

In order to know if the proposed nanoporous polymorphic phases could be synthesized, they would possess novel properties. As well as investigate the characteristic properties of the proposed hollow structures. In this section, we calculate the parameters characteristic for each of those nanoporous structures. The results obtained are in Table 1.

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

Structures	CAN	FAU	$Zn_{16}S_{16}$	SAT
Mass density (gcm^{-3})	4.527	3.179	3.384	4.174
Volume /at ($Å^3$/at)	14.25	20.21	19.54	15.92
Particle density ($10^{23}cm^{-3}$)	12.45	48.24	32.4	72.41
Coordination number	4	4	4	4
Band gap (eV)	3.292	3.000	3.066	2.616
Surface area ($Å^2$)	113.80	533.57	397.07	255.47
Pore volume ($Å^3$)	83.82	865.97	561.01	222.71
Crystal structure	Hex	Cub	Cub	Triclinic
Unit cell (atoms)	12	48	32	24
Lattice constant (*a*-*c*) (Å)	9.31 - 3.96	13.36	10.33	9.78
Average bond (Å)	2.037	2.040	2.074	2.036
Average angle Zn-S-Zn	118.3	110.4	109.2	109.3
Average angle S-Zn-S	118.1	110.2	103.5	109.3

The results in Table 1 show that in all polymorphic phases - infinite three-dimensional periodic crystal structure assembled from $(ZnS)_k$ molecules clusters (k = 9, 12, 16) with coordination numbers quaternary for all design structures, i.e. each Zn(S) atom has four nearest S(Zn) atoms to form an sp^3 hybridized bond in all phases. This result has important implications, as it leads to the polymorphic phases we proposed designed still retains the important properties of bulk ZnS materials such as: being a piezoelectric semiconductor and the properties in optical transparency to visible light. The results in Table 1 show that each structure – or depending on how the clusters are linked $(ZnS)_k$ (k = 9, 12, 16) gives us structures with completely different properties, no duplicate. This is shown as the results of specific volume, mass density, particle density, lattice constant, average bond, average angle and band gap of the nanopore structures are completely different. This result leads to the conclusion: each of these hollow nano structures has completely different mechanical and optical properties.

Here, we also detailed calculations of the porosity for low-density nanoporous structures through such quantities as pore volume, and surface area of hollow porous. The results allow us to evaluate the porosity of the nanoporous polymorphic phases that we proposed to study the design. Paying more attention to the results of the graphs in Figure 6 and 7, we can give to the conclusion: the nanoporous structures that we designed here can sustainably exist in reality. Therefore, these new nanoporous phases, if synthesized, will be one of the most promising structural candidates to replace expensive, brittle, fragile, and less elastic materials. Since the structures that we propose to study are low-density nano structures, so they possess porosity and hollow-cage structures. Therefore, these structures have many applications for containing, purifying, i.e. letting through or preventing, retaining inside its interior atoms and molecules with sizes corresponding to the hollow porous, This is a trend that is widely applied in the field of catalysis, purification, in oil refining technology, etc.

3. Conclusion

According to the results of our theoretical prediction of the candidates for ZnS nanoporous crystal structures according to the bottom-up approach, these structures are completely different. The structural, mechanical and electrical properties analyses clearly show that nanoporous phases can exist in periodic structures without collapsing the structure, which can lead to the existence of nanoporous phases and low-density crystalline materials. An important factor for practical applications is the ability to adjust the band gap, surface area and pore volume due to the influence of the configuration in the structure.

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