# Journal of Computational Methods in Molecular Design, 2012, 2 (2):68-75



Scholars Research Library (http://scholarsresearchlibrary.com/archive.html)



# Quantum chemical study of Gallium Sulphide small nanoclusters

# Apoorva Dwivedi<sup>1</sup>, Anoop Kumar Pandey<sup>1</sup>, Neeraj Misra<sup>1\*</sup>

<sup>1</sup>Department of Physics, Lucknow University, Lucknow, 226007, India.

### ABSTRACT

A DFT study of the stability, structural, electronic and vibrational properties has been performed for different gallium sulfide nanoclusters  $Ga_xS_y$  (x + y = 2 - 5). A B3LYP/6-311G(3df) method is employed to optimize the geometries The binding energies (BE), final binding energy (FBE), HOMO-LUMO gaps and the bond lengths have been obtained for all the clusters. For a fixed value of n, we designate the most stable structure the one, which has maximum final binding energy per atom. The binding energy, band gap, dipole moments, vibrational frequencies and infrared intensities have been investigated for the most stable structures. First time any theoretical studies on gallium sulphide clusters are going to be presented. The growth of these most stable structures should be possible in experiments.

Keywords- Nanoclusters, Electronic properties, Vibrational frequencies, DFT.

#### INTRODUCTION

A nanocluster is an intermediate phase between the molecule and bulk, whose electronic and other properties may be exotic [1, 2]. In nanoclusters, the surface area to volume ratio is quite high as compared to the bulk. The sizes of the electronic devices have been reduced because of this advancement [3, 4]. Gallium is a Block P, Group 13, Period 4 element. Gallium has been most widely used in the production of semi conducting compounds. Of these, the most important are the compounds of gallium with antimony, arsenic and phosphorous. Nowadays gallium arsenide (Ga-As) is undoubtedly the most important semiconductor. This compound is used in the production of several electronic parts such as diodes and transistors used for voltage rectification, signal amplification, etc. Other gallium arsenide applications are the semiconductor "lasing" and microwave generation and also in sensors to measure temperature, light or magnetic field [5]. Gallium sulfide is currently of interest as a surface passivation material for GaAs [6-9] and alkaline earth thiogallates, such as cerium-doped  $Sr_2Ga_2S_5$  which are promising materials for phosphor thin films in electroluminescent displays [10-14]. Some experimental studies have been done on gallium sulphide that shows thermal conductivity and mechanism of thin film formation [15, 16]. An understanding of the physical properties of these clusters at the atomic level is required for their possible applications in microelectronic devices. Two primary factors cause nanomaterials to behave significantly differently than bulk materials: surface effects (causing smooth properties scaling due to the fraction of atoms at the surface) and quantum effects (showing discontinuous behavior due to quantum confinement effects in materials with delocalized electrons). These factors affect the chemical reactivity of materials as well as their mechanical, optical, electric, and magnetic properties. Chemical reactivity generally increases with decreasing particle size, surface coatings and other modifications can have complicating effects, even reducing reactivity with decreasing particle size in some instances [17]. Measurements of the electrical conductivity and optical absorption coefficient were performed on thin films of gallium sulphide obtained by the evaporation of bulk single crystals onto unheated glass substrates. The conductivity

Neeraj Misra et al

below 300 K varies exponentially with  $T^{1/4}$ , indicating a variable range hopping in localized states near the Fermi level.

The dependence of the absorption coefficient on the incident photon energy shows that both direct and indirect transitions take place in gallium sulphide films [18]. Another theoretical study for the physical properties of both the surfaces and the bulk has been undertaken [19]. However, a study of the small size nanoclusters of these sulfides is still lacking. To the best of our knowledge no detailed DFT calculations have been performed on gallium sulphide nanoclusters so far.

#### 2. Computational details

The theoretical methods used in this study were based on ab-initio methods within the density functional theory [20] approximation using the three-parameter hybrid functional B3LYP [21, 22] and 6-311G (3df) as the basis set. We use the triple split valance basis set, 6-311G where one employs three sizes of the contracted functions per orbital type. The advantage of the split valance basis set is that it allows the orbitals to change their sizes without making any change in the shape of the orbitals. For overcoming this limitation, we use a polarizable basis set 6-311G (3df) by adding orbitals with the angular momentum beyond what is necessary for the description of the ground state of each atom. For S and Ga atoms we add three d functions and one f function, respectively. All calculations were performed using the Gaussian 09 software package [23].

#### **RESULTS AND DISCUSSION**

#### **3.1 Stability of structures**

Different types of structures including the linear chains, rings, planer and three-dimensional ones have been investigated.

In order to have stability of nanocluster, we define the binding energy of the nanocluster. We subtract the total energy of a nanocluster from the sum of the energies of all the isolated atoms present in the nanocluster and divide the resultant quantity by the number of atoms. We name this as the binding energy (BE) per atom. For a more precise calculation, we have calculated the harmonic vibrational frequencies and the corresponding zero point energy (ZPE) has been subtracted from the earlier calculated BE value to obtain the final binding energy (FBE) = BE - ZPE.

Among all the complexes pertaining to a specific chemical formula (isomers)  $Ga_xS_y$ , the configuration possessing the maximum value of BE is named as the most stable structure. All the possible structures are given in figure 1.

For the isolated two atoms  $S_2$ , GaS, and Ga<sub>2</sub> clusters, the bond lengths are 1.90, 2.09, and 2.59 Å, respectively. The calculated value 1.90 Å of S–S bond length is in excellent agreement with the experimental value of 1.89 Å [24]. The calculated value 2.59 Å of Ga–Ga bond length is nearly same for bulk material of GaS with the other theoretical value of 2.44 Å in the literature [19], but it is not necessary for Ga-Ga bond length in a Ga2 cluster same as it in bulk materials. One may expect the minimum energies for those complexes which contain the maximum number of the S–S bonds followed by Ga–S and Ga–Ga bonds.

We now discuss each nanocluster individually below:

For GaS, The ground state nanocluster of GaS is shown in Fig. 1. The calculated FBE is 2.69 eV. Our computed value for Ga–S bond length of 2.09 Å is slightly lower as reported by Machado- Charry et-al [19].

#### $\underline{Ga_xS_y(x+y=3)}$

We have built different structures for x + y = 3. Out of these structures we are discussing only lowest stable structures for  $Ga_2S$  and  $GaS_2$  clusters.

For Ga<sub>2</sub>S, We have considered the one linear, one bend and a triangular configuration as shown in Fig. 1. Among them, the triangular configuration (Ga<sub>2</sub>S b) is most stable having  $C_{2v}$  symmetry and the calculated FBE is 2.95 eV.

## Neeraj Misra et al

For the triangular configuration, the calculated Ga–S and Ga-Ga bond lengths are 2.29 Å and 3.99 Å as given in Table 2. Due to the lower bond length of Ga-S bond more preferable than Ga-Ga.

For GaS<sub>2</sub>, We have considered the one linear, one bend and a triangular configuration as shown in Fig. 1. Among them, the linear configuration (GaS<sub>2</sub>) is most stable having  $C_{\infty v}$  symmetry and the calculated FBE is 3.29 eV. For the linear Ga-S-Ga structure, the calculated Ga-S bond length is 2.07 Å as given in Table 2.

 $\underline{Ga_xS_y(x+y=4)}$ 



Fig-1 All the possible structures of Gallium Sulphide clusters

We have built different structures for x + y = 4. Out of these structures we are discussing only lowest stable structures for  $Ga_2S_2$ ,  $Ga_3S$  and  $GaS_3$  clusters.

For  $Ga_2S_2$ , We have studied four linear chains (GaGaSS, GaSSGa, GaSGaS and SGaGaS), a square and a zigzag structure as depicted in Fig. 1. Among them, the square geometry ( $Ga_2S_2$  a) is most stable having  $C_{2h}$  symmetry with FBE of 3.31 eV. The computed Zn–S bond length is 2.26 Å, which is nearer to the value reported by Machado-Charry et-al [19].

For Ga<sub>3</sub>S, We have considered the three different geometries as linear chain, rhombus and a trigonal as shown in Fig. 1. All the geometries have very low FBE with respect to other configurations. Among them trigonal geometry (Ga<sub>3</sub>S a) is most stable one with FBE of 2.34 eV having  $C_1$  symmetry .The calculated values of Ga–Ga and Ga–S bond lengths are presented in Table 2.

For GaS<sub>3</sub>, We have considered the three different geometries as linear chain, rhombus and a trigonal as shown in Fig. 1. Among them rhombus geometry (GaS<sub>3</sub> b) is most stable one with FBE of 3.50 eV having  $C_1$  symmetry .The calculated values of S–S and Ga–S bond lengths are presented in Table 2.

#### $\underline{Ga_xS_y(x+y=5)}$

We have built different structures for x + y = 5. Out of these structures we are discussing only lowest stable structures for Ga<sub>4</sub>S, GaS<sub>4</sub>, Ga<sub>2</sub>S<sub>3</sub> and Ga<sub>3</sub>S<sub>2</sub> clusters.

For Ga<sub>4</sub>S, We have investigated different geometries namely two linear chains (GaGaGaSGa and GaGaSGaGa), rhombus and trapezoid as shown in Fig. 1. Out of them, trapezoid geometry is considered as most stable having FBE of 3.71 eV having  $C_1$  symmetry. The calculated values of Ga-Ga and Ga–S bond lengths are presented in Table 2. For GaS<sub>4</sub>, Different geometries are considered as shown in Fig 1. Among them, the pentagonal geometry is considered as most stable having FBE of 3.69 eV having  $C_1$  symmetry. The computed values of different bond lengths are presented in Table 2. For Ga<sub>2</sub>S<sub>3</sub>, We have studied different configurations as depicted in Fig. 1. The pentagonal geometry is most stable with FBE of 3.40 eV having  $C_s$  symmetry. The calculated values of Ga–S and S–S bond lengths are 2.35 and 2.04 Å, respectively. For Ga<sub>3</sub>S<sub>2</sub>, Different structures as shown in Fig. 1 are investigated. The triangular bipyramidal geometry having FBE of 2.99 eV is found as most stable having  $C_1$  symmetry. Various predicted bond lengths are shown in Table 2.

The variation of FBE with the nanocluster size (x + y = n) for the most stable configurations has been depicted in Fig. 2. No experimental data is available for comparison.

| Nanocluster                      | Symmetry        | BE (eV.) | ZPE (eV.) | FBE (eV) | HOMO-LUMO Gap                     |
|----------------------------------|-----------------|----------|-----------|----------|-----------------------------------|
| GaS                              | $C_{\infty v}$  | 2.72     | 0.03      | 2.69     | α=5.61<br>β=3.34                  |
| Ga <sub>2</sub> S b              | C <sub>2v</sub> | 2.99     | 0.04      | 2.95     | 2.02                              |
| GaS <sub>2</sub>                 | $C_{\infty v}$  | 3.35     | 0.06      | 3.29     | α=7.20<br>β=1.63                  |
| Ga <sub>2</sub> S <sub>2</sub> a | C <sub>2h</sub> | 3.40     | 0.09      | 3.31     | 3.14                              |
| Ga <sub>3</sub> S a              | C <sub>1</sub>  | 2.38     | 0.04      | 2.34     | $\alpha = 2.55$<br>$\beta = 2.51$ |
| GaS <sub>3</sub> b               | C <sub>1</sub>  | 3.60     | 0.10      | 3.50     | $\alpha = 2.71$<br>$\beta = 2.61$ |
| Ga <sub>4</sub> S                | C1              | 3.78     | 0.07      | 3.71     | 2.44                              |
| GaS <sub>4</sub> a               | C <sub>1</sub>  | 3.82     | 0.13      | 3.69     | $\alpha = 2.41$<br>$\beta = 1.24$ |
| Ga <sub>2</sub> S <sub>3</sub> a | Cs              | 3.52     | 0.12      | 3.40     | 1.28                              |
| $Ga_3S_2 b$                      | C <sub>1</sub>  | 3.08     | 0.09      | 2.99     | $\alpha = 3.16$                   |

# Table 1 Symmetry, binding energy per atom (BE), Zero point energy (ZPE), Final binding energy (FBE) and<br/>HOMO–LUMO gap for all the stable configurations of Ga<sub>x</sub>S<sub>y</sub> (x + y = 2 to 5) nanoclusters

The final binding energy (FBE) = BE - zero point energy (ZPE).  $\alpha$ ,  $\beta$  are two types to denote band gap in indirect semiconductors.

| Nanoclusters                     | Bonds | Bond length(A <sup>o</sup> ) |
|----------------------------------|-------|------------------------------|
| GaS                              | Ga-S  | 2.09                         |
| Ga <sub>2</sub> S b              | Ga-S  | 2.29                         |
|                                  | Ga-Ga | 3.99                         |
| $GaS_2$                          | Ga-S  | 2.07                         |
| Ga <sub>2</sub> S <sub>2</sub> a | Ga-S  | 2.26                         |
| Ga <sub>3</sub> S a              | Ga-S  | 2.48                         |
|                                  | Ga-Ga | 3.20                         |
| GaS <sub>3</sub> b               | Ga-S  | 2.67                         |
|                                  | S-S   | 2.74                         |
| Ga <sub>4</sub> S                | Ga-S  | 2.48                         |
|                                  | Ga-Ga | 3.00                         |
| GaS <sub>4</sub> a               | Ga-S  | 2.50                         |
|                                  | S-S   | 2.07                         |
| $Ga_2S_3a$                       | Ga-S  | 2.35                         |
|                                  | S-S   | 2.04                         |
| $Ga_3S_2b$                       | Ga-S  | 2.63                         |
|                                  | Ga-Ga | 3.32                         |

Table 2 Bond lengths (Å) for all the most stable configurations of  $Ga_xS_y$  (x + y = 2 to 5) nanoclusters

#### 3.2 Electronic structure, Thermodynamic properties and charge on atoms

The computed HOMO-LUMO gaps for all the studied structures are included in Table 1 and their variation with the cluster size (x + y = n) for the most stable configurations has been depicted in Fig. 3. The HOMO-LUMO gap first increases up to n = 3 and then decreases for n>3 with nanocluster size. Experimental data is not available for comparison. Cluster Ga<sub>2</sub>S<sub>3</sub> a is most reactive them all because it has lowest frontier orbital band gap ie. 1.28 eV. The charge on atoms of the most stable geometries of Ga<sub>x</sub>S<sub>y</sub> nanoclusters and their dipole moments are presented in Table 3.



Fig. 2- variation of FBE with nanocluster size

![](_page_5_Figure_2.jpeg)

![](_page_5_Figure_3.jpeg)

Table 3 Charge on atoms of the most stable configurations of  $Ga_xS_y$  (x + y = 2 to 5) nanoclusters and their dipole moment (in Debye units)

| Nano clusters                    | Charges on atoms |                |                |                | Dipole moment(D) |      |
|----------------------------------|------------------|----------------|----------------|----------------|------------------|------|
|                                  | $\mathbf{q}_1$   | $\mathbf{q}_2$ | $\mathbf{q}_3$ | $\mathbf{q}_4$ | $\mathbf{q}_5$   |      |
| GaS                              | 0.346            | -0.346         | -              | -              | -                | 3.43 |
| Ga <sub>2</sub> S b              | -0.539           | 0.269          | 0.269          | -              | -                | 1.59 |
| GaS <sub>2</sub>                 | 0.429            | -0.214         | -0.214         | -              | -                | 0.00 |
| Ga <sub>2</sub> S <sub>2</sub> a | 0.313            | -0.313         | -0.313         | 0.313          | -                | 0.00 |
| Ga <sub>3</sub> S a              | 0.170            | 0.173          | 0.173          | -0.516         | -                | 1.09 |
| GaS <sub>3</sub> b               | -0.033           | 0.332          | -0.144         | -0.144         | -                | 1.86 |
| Ga <sub>4</sub> S                | 0.121            | 0.121          | 0.121          | 0.121          | -0.483           | 0.25 |
| GaS <sub>4</sub> a               | -0.204           | 0.054          | 0.054          | -0.204         | 0.300            | 0.21 |
| $Ga_2S_3a$                       | 0.365            | -0.186         | -0.186         | -0.357         | -0.186           | 0.56 |
| Ga <sub>3</sub> S <sub>2</sub> b | -0.472           | -0.473         | 0.327          | 0.327          | 0.291            | 0.24 |

#### **3.3 Vibrational frequencies**

The vibrational frequencies are calculated using B3LYP/6-311G (3df) method for the most stable nanoclusters. We have also calculated infrared intensities (IR int.). The above calculated physical quantities for all the most stable nanoclusters are presented in Table 4. The above physical properties have not been studied by any other worker. We discuss the above properties of each nanocluster below:

For GaS, We obtain the stretching mode frequency of 436 cm<sup>-1</sup> which is IR active. No experimental data is available for comparison.

For Ga<sub>2</sub>S b, Triangular GaSGa structure, the calculated frequencies are 372, 283, and 48 cm<sup>-1</sup>. The highest frequency of 372 cm<sup>-1</sup> corresponds to the breathing vibration is IR active. The frequency of 283 cm<sup>-1</sup> and 48 cm<sup>-1</sup> arises from the bending motion.

For  $GaS_2$ , for the symmetric linear SGaS structure, the calculated frequencies are 457, 408, 116, and 104 cm<sup>-1</sup>. The highest frequency of 457 cm<sup>-1</sup> corresponds to the Ga–S stretching vibration. The frequency of 408 cm<sup>-1</sup> arises from the breathing motion of the two outer S atoms. The lowest frequency modes are due to bending vibrations.

For GaS<sub>3</sub> b, rhombus SSSGa structure, the calculated frequencies are 114, 162, 211, 229, 458, 531 cm<sup>-1</sup>. The highest frequency of 531 cm<sup>-1</sup> corresponds to the S–S stretching vibration. The frequency of 162 cm<sup>-1</sup> arises from the bending motion of whole cluster.

For Ga<sub>3</sub>S a, the trigonal Ga<sub>3</sub>S structure has six vibrational frequencies in all. The low laying frequencies (30, 32, 78 cm<sup>-1</sup>) originate from Ga–Ga bonds and the high frequencies (150, 154, 307 cm<sup>-1</sup>) arise from Ga–S bonds.

For  $Ga_2S_2$  a, the square structure have six frequencies. The two high frequencies of 394 and 293 cm<sup>-1</sup> correspond to the stretching frequencies of Ga–S bonds. The lowest and highest frequencies are IR active.

For Ga<sub>4</sub>S, trapezoid structure has 9 frequencies. The low laying frequencies (59, 60, 61, 62, 95 cm<sup>-1</sup>) originate from Ga–Ga bonds and the high frequencies (116, 259, 271, 272 cm<sup>-1</sup>) arise from Ga–S bonds.

 $GaS_4$  a, pentagonal structure has 9 frequencies. The higher frequencies of 429, 500, and 518 cm<sup>-1</sup> appear due to the stretching vibrations of S atoms close to the Ga atoms.

For  $Ga_2S_3$  a, pentagonal structure has 9 frequencies. The higher frequencies of 325, 380 and 515 cm<sup>-1</sup> appear due to the stretching vibrations of S atoms close to the Ga atoms.

For  $Ga_3S_2$  b, triangular bipyramidal structure has 9 frequencies. The higher frequencies of 356 and 347 cm<sup>-1</sup> appear due to the stretching vibrations of S atoms close to the Ga atoms. The lower frequencies of 82, 106 and 146 cm<sup>-1</sup> appear due to the twisting vibrations of whole cluster.

# Table 4 The calculated vibrational frequencies (Cm<sup>-1</sup>), Infrared intensities (IR Int. in km mol<sup>-1</sup>) of the most stable configurations of $Ga_xS_y$ (x + y = 2 to 5) nanoclusters

| Nanoclusters                     | Properties     | Values   |
|----------------------------------|----------------|--|
| GaS                              | Frequencies    | 436  |
|                                  | IR intensities | 16.36  |
| Ga <sub>2</sub> S b              | Frequencies    | 48, 283, 372   |
|                                  | IR intensities | 0.33, 18.74, 278.23                                      |
| GaS <sub>2</sub>                 | Frequencies    | 104, 116, 408, 457                                       |
|                                  | IR intensities | 8.27, 6.79, 0.00, 158.05                                 |
| Ga <sub>2</sub> S <sub>2</sub> a | Frequencies    | 97, 142, 202, 293, 393, 394                              |
|                                  | IR intensities | 10.77, 6.99, 0.00, 0.00, 0.00, 38.78                     |
| Ga <sub>3</sub> S a              | Frequencies    | 30, 32, 78, 150, 154, 307                                |
|                                  | IR intensities | 0.26, 0.38, 1.16, 10.79, 10.47, 42.57                    |
| GaS <sub>3</sub> b               | Frequencies    | 114, 162, 211, 229, 458, 531                             |
|                                  | IR intensities | 3.43, 5.46, 30.93, 10.48, 0.80, 1.93                     |
| Ga <sub>4</sub> S                | Frequencies    | 59, 60, 61, 62, 95, 116, 259, 271, 272                   |
|                                  | IR intensities | 0.38, 0.38, 0.00, 0.03, 0.00, 0.00, 12.23, 69.11, 69.13  |
| GaS <sub>4</sub> a               | Frequencies    | 66, 73, 165, 182, 215, 299, 429, 500, 518                |
|                                  | IR intensities | 0.00, 2.02, 14.57, 0.01, 23.77, 0.58, 1.26, 58.44, 9.09  |
| Ga <sub>2</sub> S <sub>3</sub> a | Frequencies    | 24, 106, 117, 157, 262, 273, 325, 380, 515               |
|                                  | IR intensities | 14.53, 3.61, 0.00, 0.00, 0.02, 9.21, 1.32, 36.12, 1.21   |
| $Ga_3S_2b$                       | Frequencies    | 72, 82, 106, 146, 148, 167, 216, 347, 356                |
|                                  | IR intensities | 0.00, 0.00, 2.90, 12.46, 50.20, 1.92, 38.78, 34.56, 5.39 |

### CONCLUSION

The present study establishes the occurrence of the most stable configurations of the various GaS nanoclusters. For  $Ga_xS_y$  nanoclusters, we have predicted the bond lengths, binding energies, HOMOLUMO gaps, charge on atoms, dipole moments, vibrational frequencies, and IR intensities, which need to be verified experimentally. No experimental data is available for comparison. The FBEs of most stable clusters also increase with the cluster size n with the same number of Ga, e.g., GaS4>GaS3>GaS2>GaS, or Ga2S3a>Ga2S2>Ga2S. The HOMO-LUMO gap first increases from n = 2 to 3 but decreases after n = 3. Band gap shows the reactivity of clusters. By knowing the value of dipole moment we can conclude that the clusters having higher dipole moment can be treated as a good solvent. The study of the different vibrations of the S–S bonds. The lower frequencies belong to either Ga–S stretching or bending vibrations. We find that although some other structures have high BE's but as their low frequencies are imaginary, they may not be stable. The growth of these most stable structures should be possible in experiments.

#### Acknowledgment

The authors (NM & AD) are thankful to University Grants Commissions, New Delhi for its financial assistance.

#### REFERENCES

[1] ER. Bernstein, Atomic and molecular clusters studies in physical and theoretical chemistry, vol 68. Elsevier, Amsterdam, **1990**.

[2] P. Jena, B.K. Rao, S.N. Khanna, Physics and chemistry of small clusters (NATO ASI Series vol 158). Kluwer, Dordrecht **1990**.

[3] H.J. Himmel, N. Hebben, Chem. Eur. J, 11, 2005, 4096–4102.

[4] S.M. Sheehan, G. Meloni, B.F. Parsons, N. Wehres, D.M. Neumark, J Chem Phys, 2006, 124(6), 064303.

[5] Galium Sulfide, American Elements Products, American Elements is a U.S. Registered Trademark. ©. American Elements. All rights reserved 2001-2010.

[6] R. I. Pelzel, B. Z. Nosho, W. V. Shoenfeld, T. Lundstrom, P. M. Petroff, W. H. Weinberg, Appl. Phys. Lett. 1999, 75, 3354.

[7] X. Hu. Cao, X. Ding, Z. Yuan, Y. Dong, X. Chen, B. Lai, X. Hou, J. Vac. Sci. Technol. B 1988, 16, 2656.

[8] X. Chen, X. Hou, X. Cao, X. Ding, L. Chen, G. Zhao, X. Wang, J. Cryst. Growth, 1997, 173, 51.

[9] A. N. MacInnes, M. B. Power, A. R. Barron, P. P. Jenkins, A. F. Hepp, Appl. Phys. Lett. 1993, 62, 711.

[10] S. Okamoto, K. Tanaka, Y. Inoue, Appl. Phys. Lett. 2000, 76, 946.

[11] I. S. R. Sastry, C. F. Bacalski, J. McKittrick, J. Electrochem. Soc. 1999, 146, 4316.

[12] O. N. Djazovski, T. Mikami, K. Ohmi, S. Tanaka, H. Kobayashi, J. Electrochem. Soc. 1997, 144, 2159.

[13] S.S. Sun, R. T. Tuenge, J. Kane, M. Ling, J. Electrochem. Soc. 1994, 141, 2877.

[14] D. C. Smith, J. A. Samuels, B. F. Espinoza, E. Apen, N. M. Peachey, R. C. Dye, R. T. Tuenge, C. F. Schaus, C. N. King, Digest of 1995 SID Int. Symp., 728, **1995**.

- [15] M. A. Alzhdanov, M. D Nadzhafzade and Z. Yu. Seidov, Physics of solid state, Vol. 41, no. 1, 1999.
- [16] A N. MacInnes, M B. Power and A. R. Barron, Chem. Mater 1992, Vol. 4 No. 1.
- [17] E. Roduner, Chem. Soc. Rev. 2006, 35, 583.
- [18] G. Micocci R. Rella and A. Tepore, *Thin Solid Films*, 1989, Volume 172, Issue 2, 179-183.
- [19] Machado, Charry, Canadell, and Segura, Physical Review B, 2007, 75, 045206.
- [20] P. Hohenberg, W. Kohn, Phys. Rev. 1964, 136, 13864.
- [21] A.D. Becke, J. Chem. Phys, 1993, 98, 5648.
- [22] C. Lee W. Yang, R.G. Parr, Phys. Rev. B, 1988, 37, 785.
- [23] M. J. Frisch, G. W. Truck's et-al, Gaussian, Inc., Wallingford CT, 2009.
- [24] Huber KP, Herzberg G Constants of diatomic molecules, Van Nostrand, Reinhold, New York, 1979.