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Structural and Electronic studies on Al Substituted SnO_2 nano structures a DFT Study

Saravanakannan V *[1] and Radhakrishnan T[2]

[1]School of Electrical & Electronics Engineering, SASTRA University, Tirumalaisamudram, Thanjavur -613 401, India
[2]Department of Physics, Srinivasa Ramanujan Center, SASTRA University, Kumbakonam – 612001, India

ABSTRACT

All substituted non stoichiometric tin oxide clusters of size six molecules have been optimized for three different structure such as linear chain, circle ring and square structure to study the structural stability. The constructed clusters geometry was optimized using B3LYP exchange correlation function with LanL2DZ as basis set. In order to find the stability of the clusters, Energy, Binding Energy and vibrational analysis were studied. The other parameters such as dipole moment, HOMO-LUMO gap, Ionization potential, Electron affinity were calculated and the results are discussed.

Keywords: SnO_2 nano cluster, B3LYP,HOMO-LUMO, Binding energy.

Corresponding author

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INTRODUCTION

Transparent conducting oxides (TCOs) are interesting materials due to its electrical conductivity and optical transparency which are considered mutually exclusive. Among the TCOs, stannic oxide (SnO_2) an important wide band gap semiconductor has found many technological applications in transparent thin film electrodes, gas sensors[1-4], varistors [5-9] and opto-electronic devices [10-11] etc., Moreover different substituted and un-substituted SnO_2 nanostructured thin film forms prepared from various techniques like spray pyrolysis[12,13], sol-gel method [14,15], sputtering [16] . There are not much work have been done so for based on theoretical studies of SnO_2 and Al substituted SnO_2 clusters. However, theoretical simulation studies have been done on SnO_2 in bulk form [17-19]. In this present work**,** on the basis of Quantum chemical calculation based Density Functional Theory (DFT), three different structures (Linear chain, circular ring, Square box) of unsubstituted and Al substituted SnO_2 with the variation in the number of Al atoms of the nanostructures have been studied to know about its structural stability and electronic properties.

COMPUTATIONAL DETAILS

Three different structures such as linear, circular and square of SnO_2 and Al substituted SnO_2 are geometrically optimized through NWChem package[20] employing Becke's three-parameter hybrid functional combined with Lee-Yang-Parr correlation functional (B3LYP) method optimized with LANL2DZ basis set. The choice of the basis set is due to, for transition metals LANL2DZ basis set core potential is effective and reliable[21]. HOMO-LUMO gap calculation for different geometrically optimized SnO_2 and Al substituted SnO_2 clusters are carried out.

RESULTS AND DISCUSSION

Structure of SnO_2:Alx (x=0 to 5) nano clusters

Three different structures, such as linear chain structure(LS), circular ring structure(CS) and square structure(SS) of Al substituted SnO_2 with Al atoms of 0, 1,2,3,4 and 5 with cluster size were optimized . The optimized structures of pure SnO_2 and SnO_2: Al is shown in Fig.1 The optimized bond length for the entire structure lie between Sn and O is almost equal to 2.0Å.

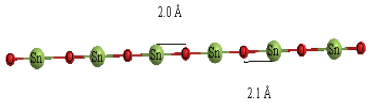

Fig. 1(a) SnO_2

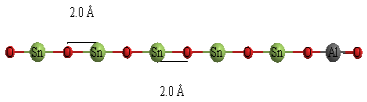

Fig. 1(b) Sno_2:Al1

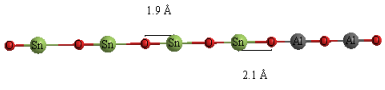

Fig. 1(c) Sno_2:Al2

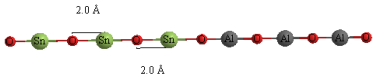

Fig. 1(d) Sno_2:Al3

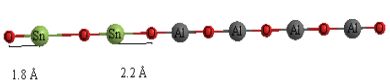

Fig. 1(e) SnO_2:Al4

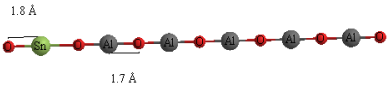

Fig.1(f) SnO_2:Al5

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Fig. 1(a-f) The optimized structures of LS - SnO_2: Alx clusters (x=0-5)

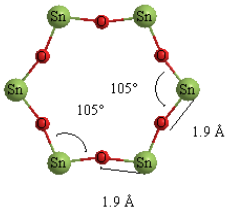

Fig.1(g) SnO_2

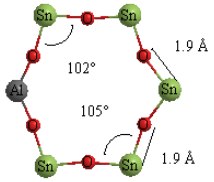

Fig.1(h) SnO_2:Al1

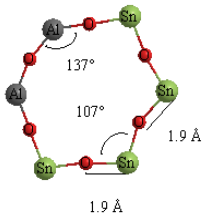

Fig.1(i) SnO_2:Al2

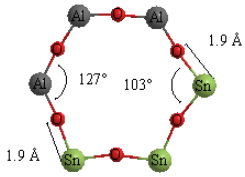

Fig.1(j) SnO_2:Al3

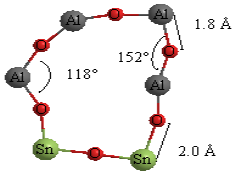

Fig.1(k) SnO_2:Al4

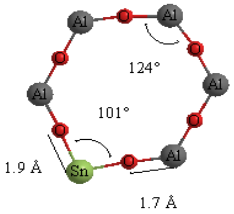

Fig.1(l) SnO_2:Al5

Fig. 1(g-l) The optimized structures of CS - SnO_2: Alx clusters (x=0-5)

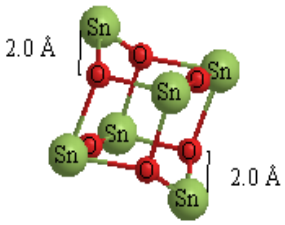

Fig.1(m) SnO_2

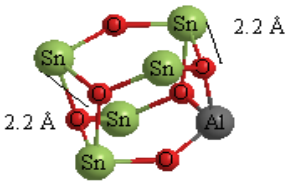

Fig.1(n) SnO_2:Al1

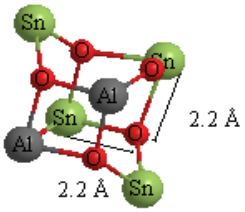

Fig.1(o) SnO_2:Al2

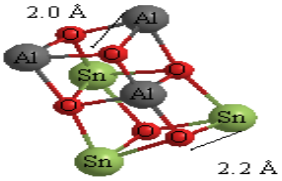

Fig.1(p) SnO_2:Al3

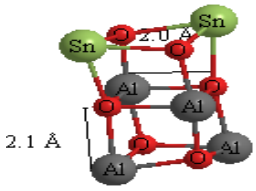

Fig.1(q) SnO_2:Al4

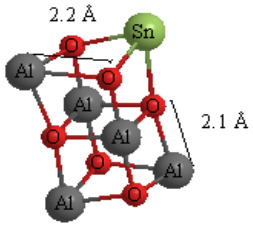

Fig.1(r) SnO_2:Al5

Fig. 1(m-r) The optimized structures of SS - SnO_2: Alx clusters (x=0-5)

The calculated energy, dipole moment and the point group symmetry of the optimized clusters are tabulated in table1. From the table data, it is seen that the obtained energy values of pure and Al substituted SnO_2 linear chain clusters, the energy value is minimum for pure SnO_2 of about -546.782 Hartrees. The substitution of Al atom in pure SnO_2 cluster increases the energy of the cluster and results the minimum stability. Increase in Al atom implies the higher in energy due to the positioning of atom. However, the calculated dipole moment of linear chain structures varies randomly with substitution of Al atom. From the obtained dipole moments, the minimum value for pure SnO_2 is about 0.3073 Debye. For Al substituted linear chain SnO_2 clusters the dipole moment varies indiscriminately, which did not produce any sequence of changes due to unbalanced charges. The symmetry observed for all linear chain structures is C_{2V} which is an unbalanced symmetry.

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Table: 1. Energy, Dipole moment (DM) and symmetry group of geometrically optimized linear SnO_2 and SnO_2:Alx nano clusters

No.	structure	Energy (Hartrees)	Dipole moment (Debye)	Point group
Linear chain				
1	SnO_2	-546.78278	0.3073	C_{2V}
2	SnO_2:Al1	-545.50166	1.8037	C_{2V}
3	SnO_2:Al2	-544.14419	15.145	C_{2V}
4	SnO_2:Al3	-542.83976	6.188	C_{2V}
5	SnO_2:Al4	-541.50688	9.5367	C_{2V}
6	SnO_2:Al5	-540.18878	2.0145	C_{2V}
Circular				
7	SnO2	-472.06653	0.0073	C_S
8	SnO2:Al1	-470.68915	1.0232	C_S
9	SnO2:Al2	-469.30901	1.7747	C_S
10	SnO2:Al3	-467.93287	2.1211	C_S
11	SnO2:Al4	-466.52208	5.127	C_S
12	SnO2:Al5	-465.17691	1.0972	C_S
Square				
13	SnO2	-472.06476	0	C_1
14	SnO2:Al1	-470.78217	0.9139	C_S
15	SnO2:Al2	-469.39747	0.8274	C_2
16	SnO2:Al3	-468.01703	4.4861	C_S
17	SnO2:Al4	-466.62505	4.9272	C_{2V}
18	SnO2:Al5	-465.25556	2.6166	C_S

From the table 1, data is seen that the obtained energy values of pure and Al substituted SnO2 circular and square clusters, the minimum energy value is obtained for pure SnO_2 of about -472.06653 and -472.06476 Hartrees respectively. The Al atom substituted in the pure SnO_2 cluster the energy increases of the closed loop cluster and the results the minimum stability due to increase in Al atom with positioning of atom. However, the dipole moment of circular and square structures varies randomly with substitution of Al atom. From the obtained dipole moments, the minimum value is for pure SnO_2 of about 0 0073 and 0 for CS and SS respectively. For Al substituted linear chain SnO_2 clusters the dipole moment varies which did not produce any sequence of changes due to unbalanced charges. The symmetry observed for all C_S point group of CS and for SS point group of C_1, C_2, C_S and C_{2V} for different Al substituted SnO_2 which is an unbalanced symmetry.

Electronic Properties of SnO2: Alx (x=0 to 5) nano clusters

The electronic properties of pure and Al substituted SnO_2 clusters are carried out in terms of the energies of highest occupied molecular (HOMO) and lowest unoccupied molecular orbit (LUMO). Table 2 shows the calculated HOMO-LUMO energies of LS, CS, SS structures of pure and Al substituted SnO_2 clusters.

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Table 2 HOMO-LUMO energy of SnO_2 and SnO_2:Alx nano clusters

No.	LS	αLUMO	αHOMO	E_g	βLUMO	βHOMO	E_g
1	Sno2	-2.59	-6.63	4.04	-4.22	-6.63	2.41
2	Sno2:Al1	-2.76	-6.54	3.78	-4.37	-6.54	2.17
3	Sno2:Al2	-3.26	-4.5	1.24	-3.22	-4.43	1.21
4	Sno2:Al3	-3.26	-4.5	1.24	-3.22	-4.43	1.21
5	Sno2:Al4	-3.76	-4.98	1.22			0
6	Sno2:Al5	-2.96	-4.94	1.98	-3.5	-5.08	1.58
No.	CS	αLUMO	αHOMO	E_g	βLUMO	βHOMO	E_g
7	Sno2	-2.08	-5.79	3.71			0
8	Sno2:Al1	-2.07	-4.72	2.65	-2.03	-5.9	3.87
9	Sno2:Al2	-2.08	-4.75	2.67	-2.44	-6.06	3.62
10	Sno2:Al3	-2.2	-4.9	2.7	-2.2	-4.9	2.7
11	Sno2:Al4	-2.85	-4.13	1.28			0
12	Sno2:Al5	-2.33	-5.07	2.74	-2.39	-5.16	2.77
No.	SS	αLUMO	αHOMO	E_g	βLUMO	βHOMO	E_g
13	Sno2	-1.77	-3.78	2.01	-4.51	-5.86	1.35
14	Sno2:Al1	-2.92	-4.7	1.78	-2.91	-6.11	3.2
15	Sno2:Al2	-2.96	-4.71	1.75	-2.95	-6.33	3.38
16	Sno2:Al3	-2.17	-5.13	2.96	-3.2	-4.72	1.52
17	Sno2:Al4	-3.11	-4.2	1.09	-3.09	-4.79	1.7
18	Sno2:Al5	-2.71	-5.29	2.58	-3.54	-5.01	1.47

From the table it is observed that almost all of the clusters are possessing alpha HOMO-LUMO due to spin up electrons and beta HOMO-LUMO due to spin down electrons in the clusters. The band gap is maximum in all the three types of clusters for pure SnO_2. The maximum band gap is observed in Al substituted LS structure is observed for SnO_2:Al5 with the value of 1.98eV. The minimum value of the band gap is observed for SnO_2:Al4 of about 1.22eV. In the case of CS structure, the same trend follows; such as SnO_2 Al5 has the maximum band gap of 2.74eV among the Al substituted SnO_2 clusters. The minimum value 1.28eV is obtained for SnO2:Al4 cluster. Among the Al substituted SnO_2 SS clusters, once again the SnO_2:Al5 has the maximum band gap of 2.58eV and SnO_2:Al4 cluster has the minimum value of 1.09eV.

Ionization Potential and Electron Affinity of SnO_2: Alx nano clusters

The Ionization potential (IP) is the amount of energy required to remove one electron from the cluster and the Electron Affinity (EA) is the amount of energy released when an electron is added with that cluster [22]. In density functional analysis, according to Koopman's theorem [23], the obtained HOMO value can be considered as IP and the LUMO value can be taken as EA.

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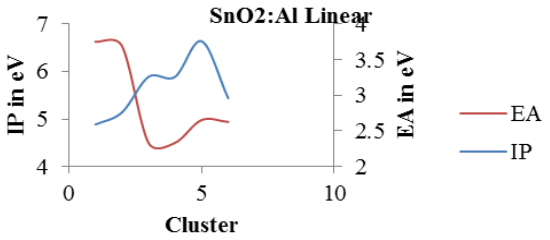

Fig.2(a)

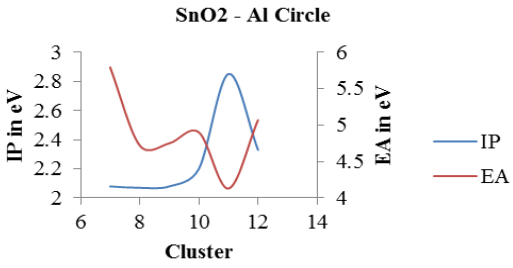

Fig.2(b)

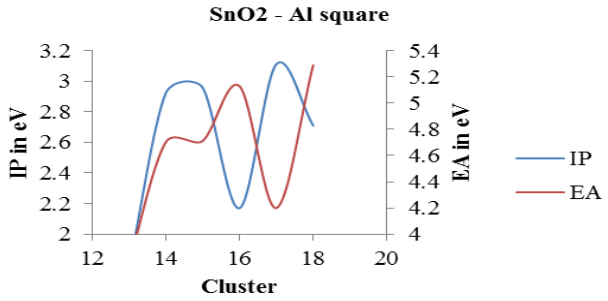

Fig.2(c)

Fig.2(a-c) Variation of Ionization Potential and Electron Affinity with SnO_2:Alx clusters

Fig 2(a),2(b) and 2(c) shows the variation of IP and EA with cluster size of three different structures of pure and Al substituted SnO_2 clusters. For LS structures, the observed IP maximum is 3.76 eV for SnO_2:Al4 and the minimum IP is observed for SnO_2:Al0 of 1.77 eV. In the case of CS structures the IP value is increases up to Al4 after that it tends to decrease. The EA curve is linearly decreasing up to Al4 and after that it tends to increase. However, From Fig 2(c), it is observed that, a zigzag variation is observed in both IP and EA for SS type structures of pure and Al substituted SnO2 clusters.

Binding energies of SnO_2:Alx nano clusters

Binding energy (BE) is one of the parameter to analyze the stability of the cluster. The binding energy of an atomic cluster has been calculated from the following formula [22]

$$BE = [(n*E(Sn)+ n*E(O)+n*E(Al) – n*E(SnOAl))/n]$$

Where n is the number of atoms, E(TM) is the energy of transition metal, E(O) is the energy of oxygen. E (TMO) is the energy of transition metal oxide in the cluster. Fig.3 shows the variation of binding energy with cluster size of three different structures of pure and Al substituted SnO_2 nano clusters.

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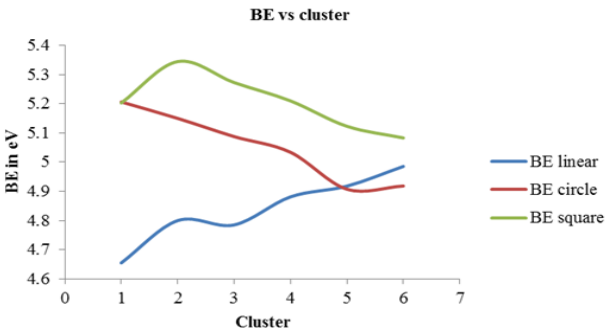

Fig. 3 Variation of binding energy with SnO_2: Alx clusters (x=0-5)

From the obtained plot, it is seen that, among the three different structures, SS structures are having higher value of binding energies and can be considered for higher stability. The CS structure has decreasing trend in binding energy when Al substitution increases. In the case of LS structure the binding energy values are increased with the substitution of Al atom.

The maximum value of BE for SS BE SnO_2:Al1 cluster is calculated for 5.344 eV and the minimum value is about 4.654eV for CS BE SnO_2:Al0 clusters as in Fig.3. In general, the BE of SS is high as well as the BE of the CS is gradually degrees and BE of LS is gradually increase with increase the Al concentration.

Vibrational Analysis of SnO_2:Alx nano clusters

Vibrational analysis of a cluster is also a deciding factor to check the stability. The vibrational analysis is studied for SnO_2: Alx nano clusters for different structure. Interestingly, irrespective of cluster structure (LS, CS and SS) all the clusters exhibit real frequency intensity and they are taken into account for stability calculation. Fig 4 (a), (b), (c), (d), (e) and (f) shows the vibrational spectrums obtained from density functional calculation for SnO_2:Alx. Interestingly, all the vibrations are due to Molecular stretch except few. The intensity value for linear SnO_2:Al1 structure is 6329.09 cm^{-1} obtained at a frequency of 472.679 cm^{-1}.

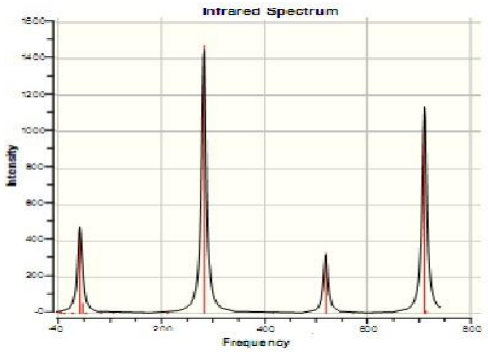

Fig.4(a) LS SnO_2

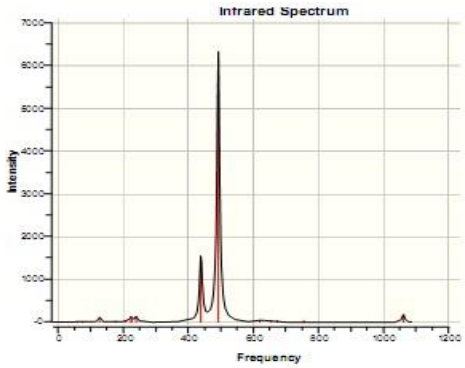

Fig.4(b) LS SnO_2:Al1

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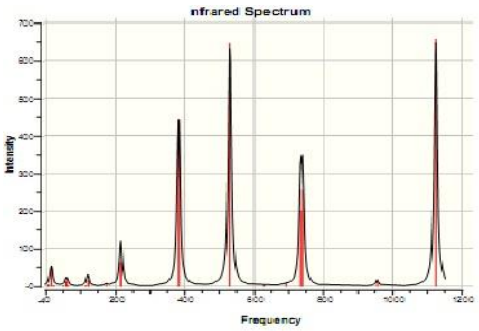

Fig.4(c) LS SnO_2:Al2

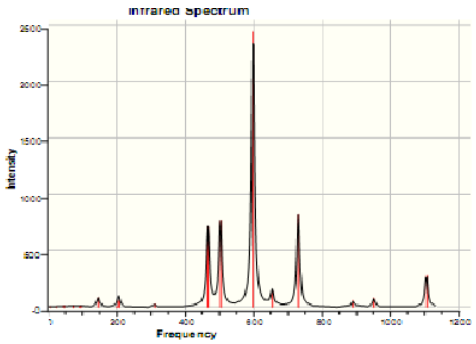

Fig.4(d) LS SnO_2:Al3

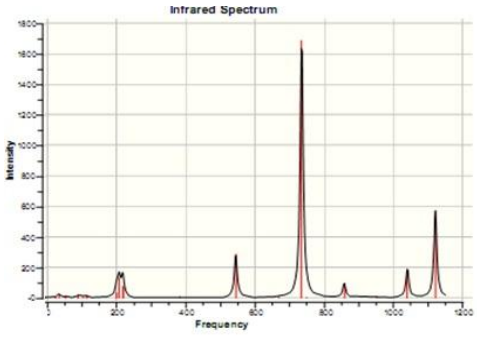

Fig.4(e) LS SnO_2:Al4

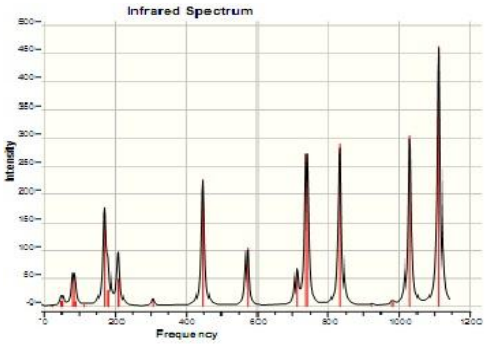

Fig.4(f) LS SnO_2:Al5

Figure 4(a-f) Vibrational spectrum of LS - SnO_2:Alx cluster

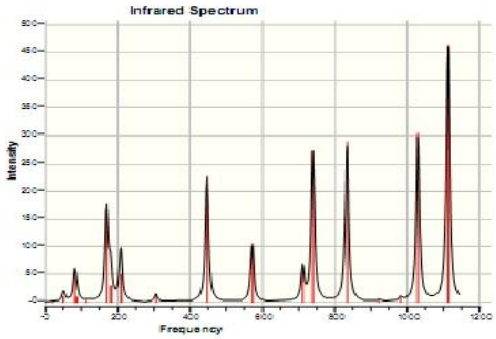

Fig.4(g) CS SnO_2

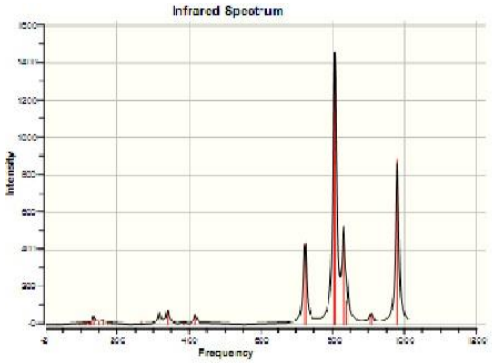

Fig.4(h) CS SnO_2:Al1

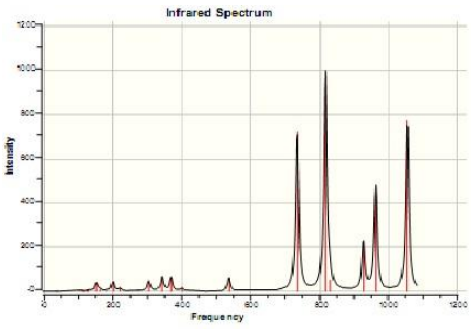

Fig.4(i) CS SnO_2:Al2

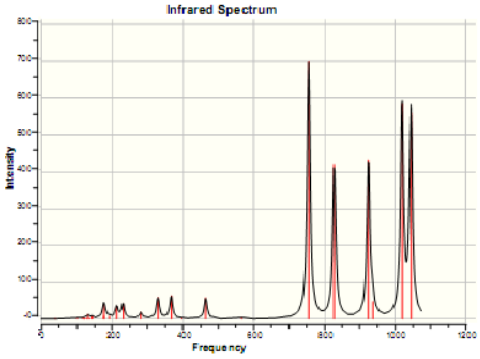

Fig.4(j) CS SnO_2:Al3

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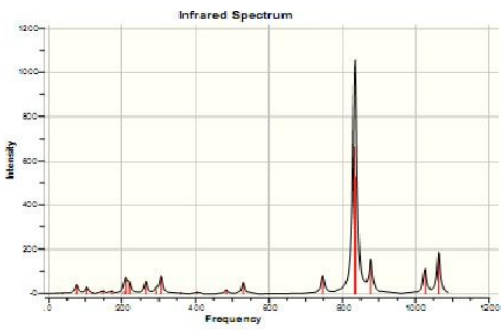

Fig.4(k) CS SnO_2:Al4

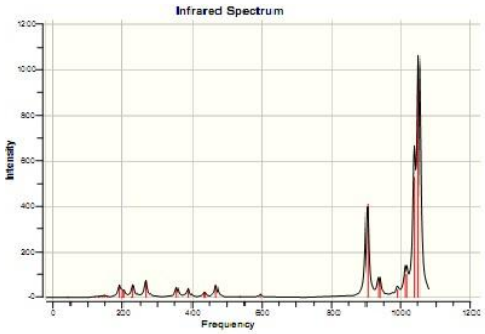

Fig.4(l) CS SnO_2:Al5

Figure 4(g-l) Vibrational spectrum of CS - SnO_2:Alx cluster

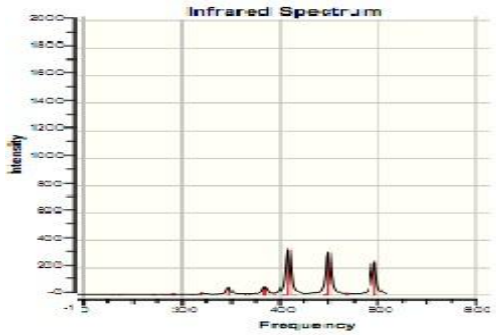

Fig.4(m) SS SnO_2

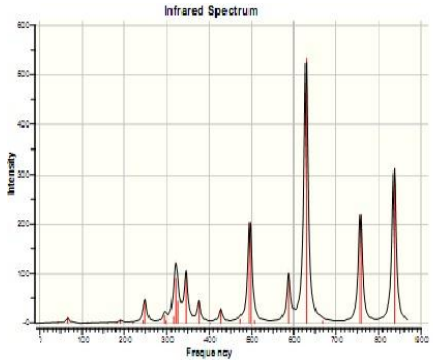

Fig.4(n) SS SnO_2:Al1

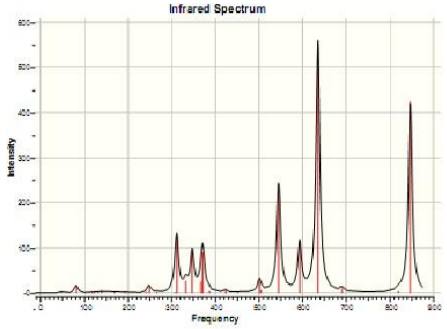

Fig.4(o) SS SnO_2:Al2

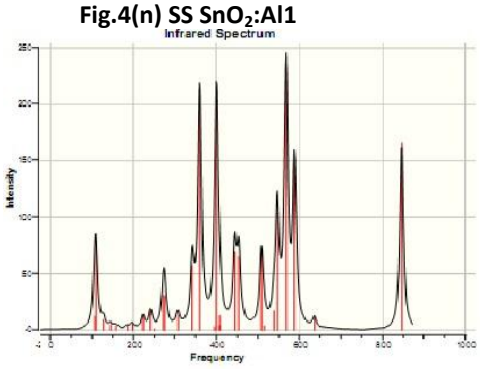

Fig.4(p) SS SnO_2:Al3

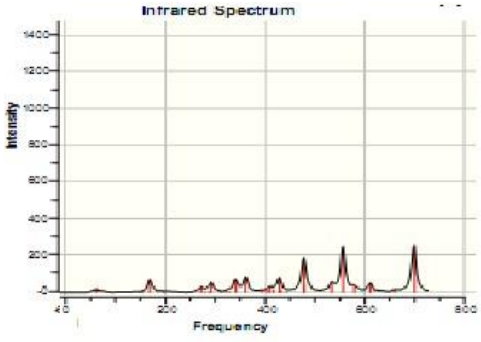

Fig.4(q) SS SnO_2:Al4

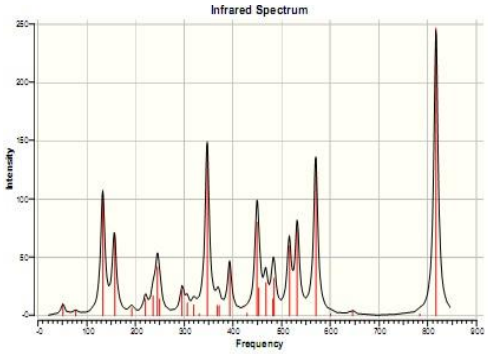

Fig.4(r) SS SnO_2:Al1

Figure 4(m-r) Vibrational spectrum of SS - SnO_2:Alx cluster

This is the maximum value of intensity obtained in this type of structure. When the Al substitution increases, the intensity value decreases. The minimum intensity value is

obtained for SnO_2:Al5 with the value of 462.396. For CS structures, the maximum intensity value is obtained for SnO_2:Al1 of about 1439.94 at 806.81. In the case of SS structure, the maximum intensity is observed for SnO2:Al2 of about 558.229 at a frequency of 635.012cm^1

CONCLUSION

The structures of the pure and Al substituted SnO_2 with Alx (x=1-5) for its different structure like linear, circle and square structures were fully optimized with B3LYP/6-31G basis set with NWChem package to find out its structural stability. The energy and dipole moment of geometrically optimized SnO_2: Alx small clusters were found and discussed. Various parameters involved in stability calculation such as binding energy, vibrational analysis were carried out for the pure and Al substituted SnO_2 clusters. From the calculated results, it is found that Square structure (SS) have greater stability compared to Linear structure (LS) and Circular structure (CS). Electronic properties such as HOMO-LUMO gap, ionization potential and electron affinity were calculated and discussed.

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