

DFT study on structural stability and electronic properties of CuO and Al substituted CuO nanoclusters

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Abstract: The realistic nanostructures such as ring, cube and sheet clusters of Copper oxide and Aluminum substituted copper oxide are optimized using density functional theory to study the structural stability. The designed nano clusters are optimized using B3LYP exchange correlation function with LanL2DZ basis set. The stability of Nano clusters is determined by calculated energy, binding energy and vibrational analysis. The other parameters such as dipole moment, HOMO-LUMO gap, Ionization potential, Electron affinity are also calculated and the results are discussed. The result will give the insights to tailor the most stable nanoclusters which find its importance in engineering applications.

Keywords: CuO, Nano cluster; HOMO-LUMO; binding energy.

Introduction

Cupric oxide (CuO) as in mineral is known as tenorite. CuO is one of the p-type semiconductors with band gap of 1.2 – 1.8 eV [1,2]. The development of p-type transparent conducting oxides is one of the key technologies for enabling p-n junction based oxide devices such as diodes, transistors and light emitting diodes. CuO and Cu₂O materials are known to be p-type semiconductors in general and hence potentially useful for constructing junction devices such as PN junction diodes [3]. Apart from their semiconductor applications these materials have been employed as solid state gas sensors and microwave dielectric materials, in addition to photovoltaic devices [4,5] copper oxide has been used as an electrode material for lithium batteries [6,7]. Delafossite like compounds are known to have interesting luminescence properties and find its applications in catalysis and they have received renewed interest with the synthesis of CuAlO₂ thin films that exhibit both p-type conductivity and also highly transparent [8]. In the present work different realistic structures of CuO nanoclusters are designed and their structural stability and electronic properties are reported.

Computational Details

The different structures of CuO and Al-CuO (Al-CuO) are geometrically optimized through Gaussian 09 package [9] employing Becke's three-parameter hybrid functional combined with Lee-Yang-Parr correlation functional (B3LYP) method optimized with LANL2DZ basis set [10-12]. HOMO-LUMO gap calculations for different geometrically optimized CuO and Al-CuO clusters are carried out using Gauss sum 3.0 packages [13]. Usually in quantum chemical calculations, the pseudopotential approximation [14] is used to replace the complex effects of bound electrons in the atoms and the effective potential of the nucleus will have a modified

potential term. Looking at the point group, except CuO ring1 cluster all other clusters belongs to C_1 symmetry group.

Results and Discussion

Structural stability of CuO and Al substituted CuO nanoclusters

The different structures, such as CuO ring and cube clusters and Al-CuO ring, cube, and sheet structures are optimized. The optimized structures of CuO and Al-CuO is shown in Figure.1. The optimized bond length for all among in the entire structure is almost equal to 2.0 Å.

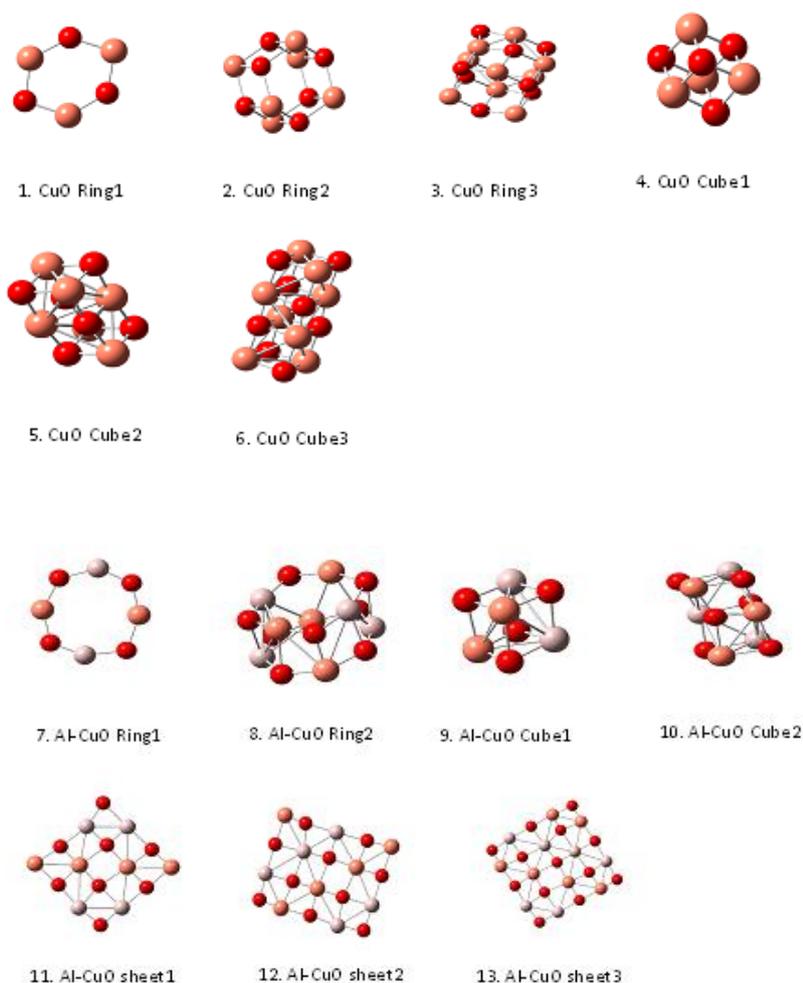


Figure.1.The optimized structures of CuO and Al substituted CuO clusters

The calculated energy, dipole moment and the point group symmetry of optimized clusters are tabulated in Table 1. Having observed the point group, all the nano clusters possess that C_1 symmetry except CuO ring1 which lies on C_5 symmetry. The ring and cube structures of CuO show an increasing trend in the energy value with increase in the number of atoms resulting increase in stability. When the number of atom increases in CuO structure, it leads to increase in stability. In the case of Al-CuO structure, the stability decreases due to substitution of Al. However, the calculated dipole moment of different structures varies randomly with either increasing the number of atoms or substitution of Al atom that may be due to geometrical arrangement. From the obtained dipole moments of CuO nano clusters, the dipole moment for CuO ring2 is found to be low in the order of 0.5059 Debye which implies that the charge distribution are almost even. In the case of, Al-CuO clusters, the dipole moment varies indiscriminately, which has not produce any sequence of changes due to unbalanced charges

Table.1 Energy, Point symmetry and Dipole moment of CuO and Al substituted CuO nanostructures

No.	Structure	Energy (Hartree)	Dipole moment (Debye)	Point group
1	CuO ring1	-5146.35	2.3356	C _s
2	CuO ring2	-10292.60	0.5059	C ₁
3	CuO ring3	-2441.57	8.1019	C ₁
4	CuO cube1	-1085.42	0.0142	C ₁
5	CuO cube2	-1625.46	0.3159	C ₁
6	CuO cube3	-2165.60	0.9824	C ₁
7	Al-CuO ring1	-693.21	1.8920	C ₁
8	Al-CuO ring 2	-8027.36	4.6706	C ₁
9	Al-CuO cube1	-692.84	5.0880	C ₁
10	Al-CuO cube2	-1045.29	2.4770	C ₁
11	Al-CuOsheet1	-1394.22	1.0800	C ₁
12	Al-CuOsheet2	-1742.43	5.6690	C ₁
13	Al-CuOsheet3	-2165.70	1.9840	C ₁

Electronic Properties of CuO and Al substituted CuO nano clusters

The electronic properties of CuO and Al-CuO clusters are designed in terms of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The range of Density of States (DOS) (Fig.2) values provides perceptivity to density of charge along the Fermi level. Location of charge near a Fermi level with small HOMO- LUMO gap will enable easier movement of electrons to the valance band. The study of the higher atomic structure of CuO and Al-CuO clusters unveil greater location of charge near the Fermi level. It should also be noted that more states are seen in the virtual orbital. This may due to placing of the atom gives rise to the localization of charge in the virtual orbital. Table 2 shows the calculated HOMO-LUMO energies of CuO and Al-CuO clusters. Interestingly the HOMO-LUMO gap decreases with increasing the cluster size, because overlapping of the Cu '4s' orbitals and O '2p' orbitals, hence the band gap decreases. From the Fig. it is observed that CuO ring1 and CuO ring3 clusters are exhibit alpha and beta energy bands due to spin up and spin down electrons. From the Table-2, in the CuO ring cluster the band gap varies arbitrarily with increase in number of atoms. For CuO cube cluster, increasing the number of atom results in decrease in the band gap.

Table.2 HOMO-LUMO gap of ofCuO and Al substituted CuO nanostructures

No.	Structure	HOMO	LUMO	E _g	No. of atoms
1	CuO ring1	-4.83	-3.00	1.83	6
2	CuO ring2	-4.31	-3.10	1.21	12
3	CuO ring3	-5.76	-4.71	1.05	18
4	CuO cube1	-6.71	-4.83	1.88	8
5	CuO cube2	-4.91	-3.37	1.54	12
6	CuO cube3	-4.65	-3.53	1.12	16
7	Al-CuO ring1	-6.02	-3.72	2.3	8
8	Al-CuO ring 2	-6.17	-3.73	2.44	16
9	Al-CuO cube1	-5.83	-3.78	2.05	8
10	Al-CuO cube2	-5.08	-3.12	1.96	12
11	Al-CuOsheet1	-4.95	-2.98	1.97	16
12	Al-CuOsheet2	-5.83	-3.01	2.82	20
13	Al-CuOsheet3	-6.03	-3.40	2.63	25

Figure.2 represents the HOMO-LUMO energy gap of CuO and Al-CuO clusters. In the case of CuO nano clusters, the high band gap of 1.88eV and 1.83eV are observed for CuO cube1 and CuO ring1 clusters respectively. The higher band gap restricts the movement of electron from HOMO to LUMO that will not actively take part in electrical conductivity.

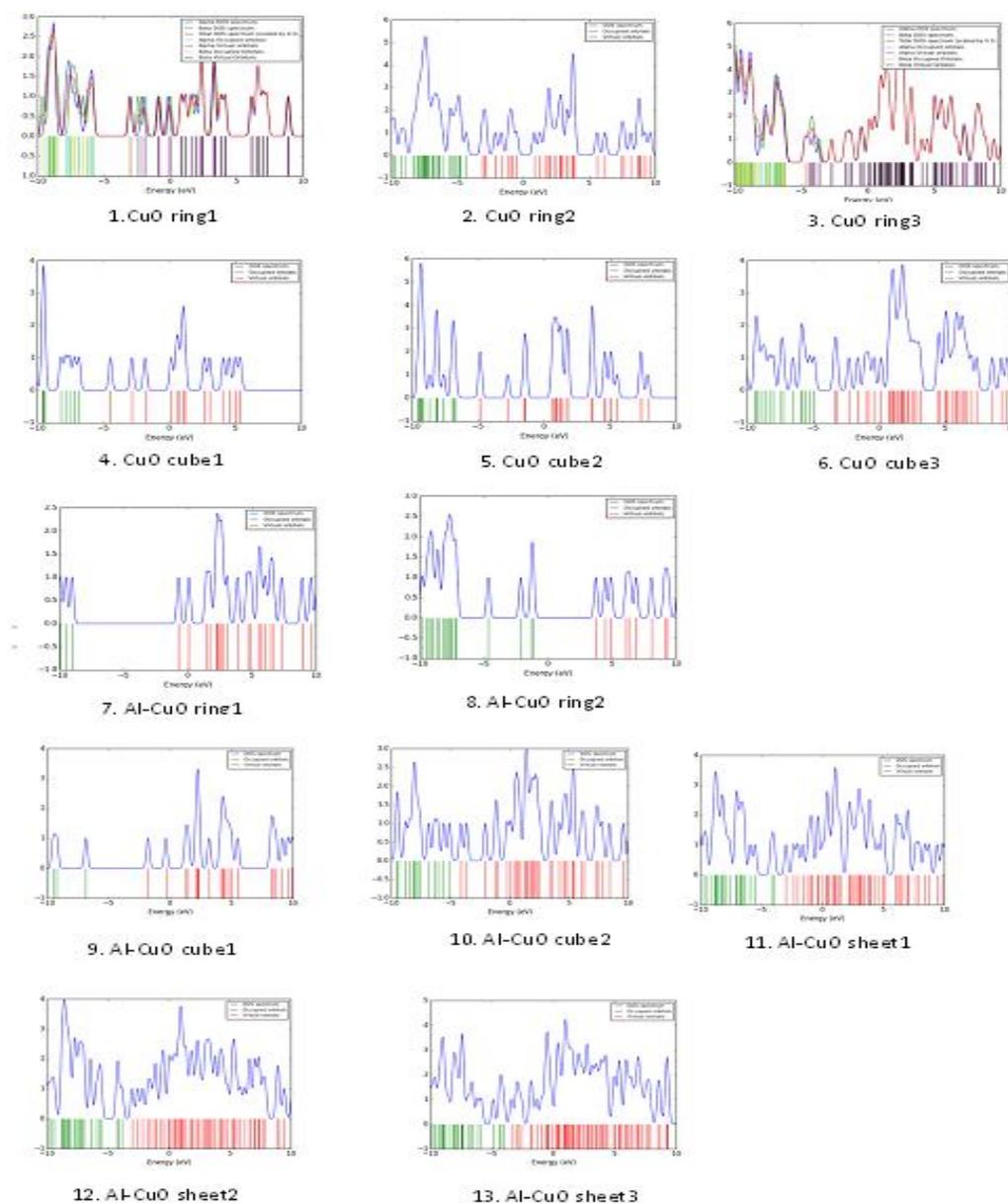
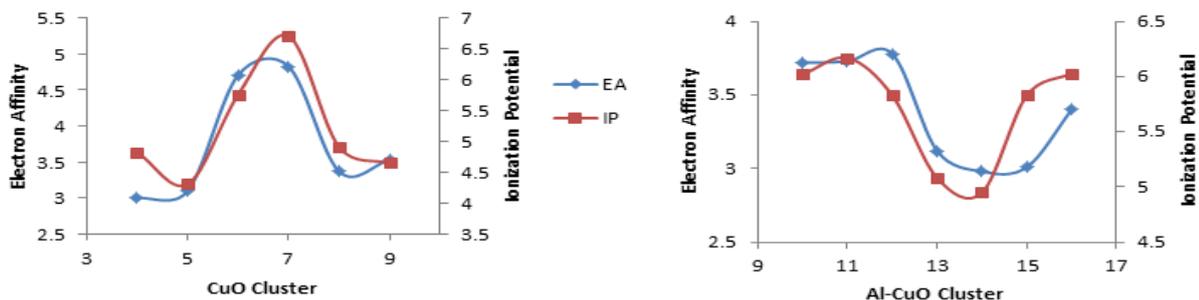


Figure.2 DOS, HOMO-LUMO energy diagram of CuO and Al-CuO

The CuO ring3 and CuOcube3 clusters have a low value gap of 1.05eV and 1.12eV respectively due to increasing the number electrons that have an active involvement in electrical conductions. In Al-CuO, the large HOMO-LUMO gaps implies that the structures are chemically inert because it is unfavorable to add electrons to a high lying LUMO level or to remove electrons from a low-lying HOMO level [15, 16]. In contrast the band gap increases with increasing the number of atom in Al-CuO clusters comparable with CuO clusters. From the result, it is found when Al is substituted in the CuO cluster, the energy gap increases which are responsible for transparency for the material [17]. From table 2, the calculated value of the energy gap shows that all clusters lie in the category of semiconductors.

Ionization Potential and Electron Affinity of CuO and Al substituted CuO nanoclusters

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 [18, 19]. In density functional analysis, according to Koopman's theorem [20], the obtained HOMO value can be considered as IP and the LUMO value can be taken as EA. Figure.3 shows the variation of IP and EA with cluster size for different structures of CuO and Al-CuO clusters respectively. For CuO clusters, the observed maximum IP is 6.71eV is for CuOcube1 and the minimum IP is observed for CuO ring2 which is 4.31eV.

Figure.3 Variation of IP and EA with CuO and Al substituted CuO clusters

However, the IP of different CuO ring structures varies randomly with increasing the number of atom. In the case of CuO cube structure, increasing the number of atoms results gradual decrease in the IP value. For Al-CuO nanocluster the observed maximum IP is for Al-CuO ring2 which is 6.17eV, having number of atoms 16 and the minimum IP is observed as Al-CuO sheet1 of 4.95eV having the same number of atoms. Increase in Al atom entails the higher in energy due to the positioning of atom. The trend of IP for CuO and Al-CuO cube clusters possesses a zigzag path. The high value of EA indicates that the cluster has an active involvement in chemical reactions. Among all the clusters, the CuO ring3 and CuO cube1 clusters have 4.71eV and 4.83eV respectively which are highly reactive. In the structure of Al doped CuO has a wide gap, which is chemically harder than the CuO clusters.

Binding energies of CuO and Al substituted CuO nano clusters

Binding energy (BE) is one of the parameters to analyze the stability of the cluster. The binding energy of an atomic cluster has been calculated from the following formula [21]

$$BE = [(n * E(Cu) + n * E(O) + n * E(Al)) - n * E(Al-CuO)] / n$$

Where n is the number of atoms, E(Cu) is the energy of Copper, E(O) is the energy of oxygen, E(Al) is the energy of Aluminum and E(Al-CuO) is the energy of Aluminum substituted Copper oxide in the cluster.

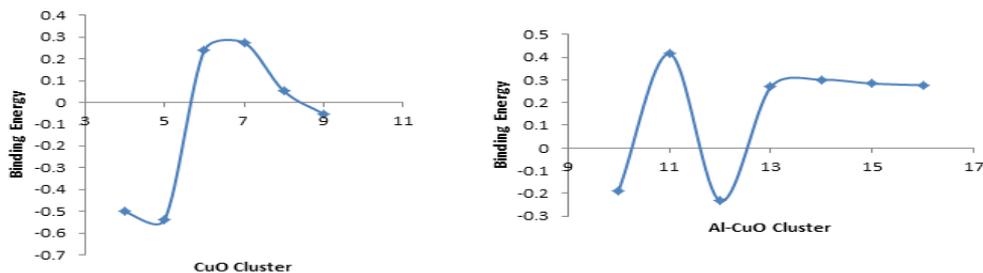
**Figure.4 Variation of BE with CuO and Al substituted CuO clusters**

Figure.4 shows the variation of binding energy with cluster size of three different structures of CuO and Al-CuO nanoclusters. From the plot, it is seen that, among different structures, Al-CuO structures are having higher value of binding energies than all CuO cluster and can be considered for higher stability. The maximum value of BE Al-CuO ring2 cluster is calculated for 0.4148eV and the minimum value is about -0.53675eV for CuO ring2. Even the number of atoms are same, the BE varies with structural formation of either enhancing the number of atoms or increasing of Al atom.

Conclusion

The structures of the CuO and Al substituted CuO for its different structure like ring, cube and sheet clusters were fully optimized with B3LYP/6-31G basis set with Gaussian 09W package to find out its structural stability. The energy and dipole moment of geometrically optimized CuO and Al substituted CuO small clusters were found and discussed. Various parameters involved in stability calculation such as binding energy carried out for the pure and Al substituted CuO clusters. From the calculated results, it is found that Al substituted CuO have greater stability compared with CuO clusters. Electronic properties such as HOMO-LUMO gap, ionization potential and electron affinity were calculated and discussed.

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