

A DFT Study on Alkali and Alkaline Earth Metal Encapsulated Fullerene-Like BeO Cluster

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ABSTRACT. By using Density Functional Theory (DFT), we have performed alkali metal and alkaline earth metal inside fullerene-like BeO cluster (FLBeOC) in terms of energetic, geometric, charge transfer, work function and electronic properties. It has been found that encapsulated processes of the alkali metal are exothermic and thermodynamically more favorable than alkaline earth metal encapsulation, so that interaction energy (E_{int}) of the alkali metal encapsulation FLBeOC is in the range of -0.02 to -1.15 eV at level of theory. It is found that, the electronic properties of the pristine fullerene-like BeO cluster are much more sensitive to the alkali metal encapsulation in comparison to alkaline earth metal encapsulation. The alkali and alkaline earth metal encapsulated fullerene-like BeO cluster systems exhibit good sensitivity, promising electronic properties which may be useful for a wide variety of next-generation nano-sensor device components. The encapsulation of alkali and alkali earth metal may increase the electron emission current from the FLBeOC surface by reducing of the work function.

Key words: Fullerene-like BeO cluster, Alkali and alkaline earth metal, Encapsulation, Density functional theory

INTRODUCTION

Due to their potential application, unique electrical, mechanical and thermal properties, the search for carbon nano-materials such as carbon nanotube (CNTs),¹ fullerene and cage has attracted great attention.²⁻⁵ Nowadays, much of the interest in nanomaterial is redirected to inorganic nanomaterial. Moreover, recently a considerable number of non-carbons such as BN and SiC,⁶⁻⁸ have been prepared and some other ones such as BeO have been reported theoretically.^{9,10}

The properties of metal oxides have been widely studied^{11,12} metal oxides have a wide range of electronic, chemical, and physical properties that are often sensitive to changes in their chemical environment and frequently the properties of the sensor are based on suitably structured and doped oxides.^{13,14} As an exceptional member of alkaline-earth oxides, beryllium oxide (BeO) can be an important covalent component in the initially ionic Be-O bond.¹⁵ Additionally, the energy gap (E_g) between the highest occupied molecular orbital and lowest unoccupied molecular orbital is one of an important effective factors on the structural stability. It keeps its properties in the cluster of bulk, while, the E_g of all structures are large.¹⁶ Mechanical and physical properties of beryllium oxide arising of distinct bonding feature in BeO consist of high hardness, melting point and

thermal conductivity as well as large elastic constants.^{17,18}

Beryllium oxide is known for having a wide range of applications including semiconductors and as being use moderator in nuclear reactors,¹⁹ optoelectronic devices²⁰ and etc. The properties of BeO often are different from carbon nanotubes such as BN and SiC. For example, the band gap of BeO nanotube (BeONT) is larger than that of SiC and BN nanotubes.²¹ Furthermore, BeO wurzite-type structure shows many different properties of covalent solids in compare with other alkaline earth, so that the Be and O atoms are bound together by sp^3 hybridized bonds,²² and also BeO wurzite-type is an insulator with wide band gap.

Since the report of the first discovery fullerenes,²³ the field of the cluster fullerenes has aroused great interest among scientific because of its unique chemistry and technological applications.^{24,25} The versatility of fullerene molecules has led to a large amount of research exploring their properties. The discovery of fullerenes was soon followed by the encapsulated atom or molecule, that is, endohedral metallofullerenes and non-metallofullerenes have been developed dramatically.²⁶⁻²⁹ Encapsulation of one or more metal atom inside a hollow cage-like structure, causes endohedral metallofullerenes to illustrate a novel functionalized molecular compound.³⁰ However, BeO nanomaterial such as BeO nanotube, BeO nanowire, BeO fullerene and cage have been investigated.^{17,22,31-33}

In the present study, we have reported a theoretical study on the interaction of four alkali metal group IA (AM) (Li, Na, K, Rb) and four alkaline earth group IIA (AEM) (Be, Mg, Ca, Sr) with fullerene-like BeO cluster using density functional theory (DFT), in terms of energetic, structural, and electronic properties. The main purpose is finding out more about the interactions between these atoms and the FLBeOCs and also the response of the fullerene-like towards these atoms. It is necessary for the possibility of the experimental investigation of novel Be₂₄O₂₄. We hoped findings of this study would provide experiments with instructive information, thus contributing to a joint experiment and theory study.

COMPUTATIONAL METHOD

Geometry optimizations and density of states (DOS) have been performed on a fullerene-like BeO cluster, and different X-encapsulated FLBeOC (X@FLBeOC) complexes (X = Li, Na, K, Rb, Be, Mg, Ca and Sr).

All calculations are carried out using density functional theory via GAMESS suite of program³⁴ and Gaussian 03 package³⁵ by using M06-2X functional³⁶ with 6-311G(d, p) and LANL2DZ basis sets³⁷ to predict the equilibrium geometries of FLBeOC and X-encapsulated fullerene-like BeO cluster. The M06-2X density functional has been commonly used in nanostructure studies^{38,39} and the M06-2X functional enhances the adsorption mechanism, which is one of the best hybrid functional among all presently available functional.⁴⁰ GaussSum program⁴¹ was used to obtain density of states (DOS) results. LANL2DZ basis set has widely been used to calculate the equilibrium geometrical properties of clusters.⁴²⁻⁴⁴

The interaction energies (E_{int}) of endohedral complexes were evaluated by comparing the energy of endohedral derivatives with the sum of the energies of the isolated components as follows:

$$E_{\text{int}} = E(\text{X@FLBeOC}) - E(\text{FLBeOC}) - E(\text{X}) \quad (1)$$

which $E(\text{X@FLBeOC})$ denote the total energy of X-encapsulated BeO fullerene-like, $E(\text{BeO})$ and $E(\text{X})$ denote the total energy of isolated FLBeOC and X atom (alkali and alkaline earth atoms), respectively. The negative E_{int} indicates that the encapsulation process is exothermic and the complex is energetically favorable.

Furthermore, the gap energy (E_g) has been defined as follows

$$E_g = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (2)$$

where E_{LUMO} and E_{HOMO} are energy of HOMO and LUMO. In the open shell systems E_{HOMO} was replaced by E_{SOMO} (SOMO = Singly Occupied Molecular Orbital). When we evaluate the properties of the sensor, the change of E_g defined by

$$\Delta E_g = (E_{g2} - E_{g1})/E_{g1} * 100 \quad (3)$$

where E_{g1} and E_{g2} are, the initial values of the E_g and encapsulation complex, respectively.

Also, following equation for the chemical potential (μ) is obtained by

$$\mu = (E_{\text{HOMO}} + E_{\text{LUMO}})/2 \quad (4)$$

The work function (ϕ) can be written as:⁴⁵

$$\phi = E_{\text{LUMO}} - \mu \quad (5)$$

The distribution of charges is calculated according to the recipe given by Mulliken based on calculation of wavefunction in molecular system.⁴⁶

Assuming normal to the Fermi level is that in a molecule (at $T = 0$ K) it lies approximately in the middle of the E_g . It is should be noted that, in fact, what lies in the middle of the E_g is the chemical potential, and because the electrons chemical potential of a free gas as is Classical definition equal to its Fermi level, here we consider, center of band gap as a Fermi level.

RESULT AND DISCUSSION

Structural Geometry

As shown in *Fig. 1* the fullerene-like Be₂₄O₂₄ cluster has been made of six octagons, eight hexagons and twelve tetragons. The angles in tetragons, hexagons and octagons vary from 81.8° to 97.7°, from 115.6° to 122.7° and from 132.1° to 134.2°, respectively. Structurally, three different types of Be–O bonds are observed within the fullerene-like; the first one is between octagonal and hexagonal, the second is between octagonal and tetragonal and the third one is between a hexagonal and a tetragonal, with average bond lengths of 1.50, 1.55 and 1.59 Å, and respectively, in accordance with previously reported values of BeO nanomaterial.⁴⁷ The range of calculated harmonic frequencies is from 92.48 to 1273.37 cm⁻¹, indicating that the structure is a true stationary point on the potential energy surface.

Mulliken charge shows a charge transfer of about 0.03 |e| of the Be atom to its neighboring O atoms in the surface of the cluster, which represents the ionic character of the Be–O bonds. The cations (Be atoms) and anions (O atoms) move inward and outward the fullerene-like surface, so that the

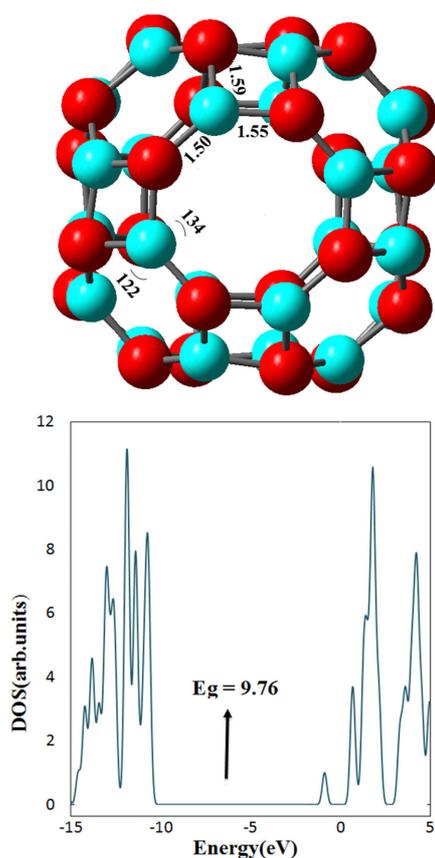


Figure 1. Geometrical parameters of pristine fullerene-like $\text{Be}_{16}\text{O}_{16}$ and its density of state (DOS) plot. Distances are in Å and angles in degree. The aqua and red balls denote Be and O atoms, respectively.

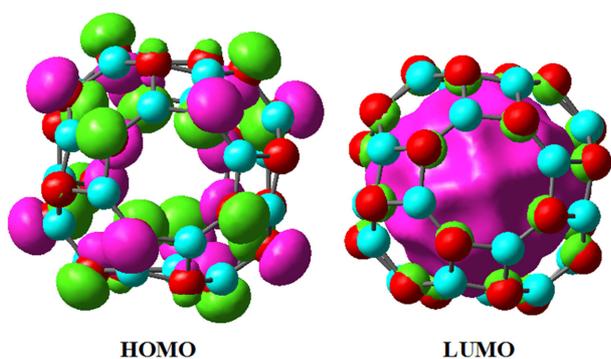


Figure 2. HOMO and LUMO of pristine fullerene-like $\text{Be}_{24}\text{O}_{24}$.

total energy of the system decreases since the electron–electron repulsion is lowered.

The DOS plot shows that the fullerene-like $\text{Be}_{24}\text{O}_{24}$ cluster is an insulator with a HOMO/LUMO energy gap (E_g) of 9.76 eV. Profiles of HOMO and LUMO of the cluster have been shown in *Fig. 2*, indicating that HOMO located mainly on the O and LUMO located on the Be atoms.

We first investigated the encapsulation of alkaline earth

metals atoms inside fullerene-like $\text{Be}_{24}\text{O}_{24}$ cluster, which was demonstrated to be energetically and vibrational stable.¹⁶

Structure Stability and Binding Energies

The formation of a BeO fullerene-like is exothermic. In order to determine the stability of the structure, we calculated binding energies using the following formula:⁴⁸

$$E_b = \frac{[E(\text{BeO})_n - n \times E(\text{BeO})]}{n} \quad (6)$$

where $E(\text{BeO})_n$ and $E(\text{BeO})$ illustrate the total energies of the $(\text{BeO})_n$ cluster and a single BeO molecule, respectively. The amount of negative E_b shows that the cluster formation is exothermic and stable. The computed binding energy of the BeO cage is -7.01 eV/atom compared with -6.846 eV/atom and -7.07 eV/atom of nano-sheet and wurtzite BeO, respectively.¹⁷ From these results, we suggest this structure is stable.

Alkaline Earth Metal (AEM) Encapsulation Fullerene-Like BeO Cluster (FLBeOC)

In order to investigate encapsulated behavior of Be, Mg, Ca and Sr inside the fullerene-like BeO, we have located different initial encapsulation sites. To find the most stable structure of endohedral fullerene-like AEM@FLBeOC, we have investigated three inner paths. Each path starts from the fullerene-like center of $\text{Be}_{24}\text{O}_{24}$, such as center of tetragonal, hexagonal and pentagonal rings. Interestingly, after full optimization, corresponding to each atom that encapsulated

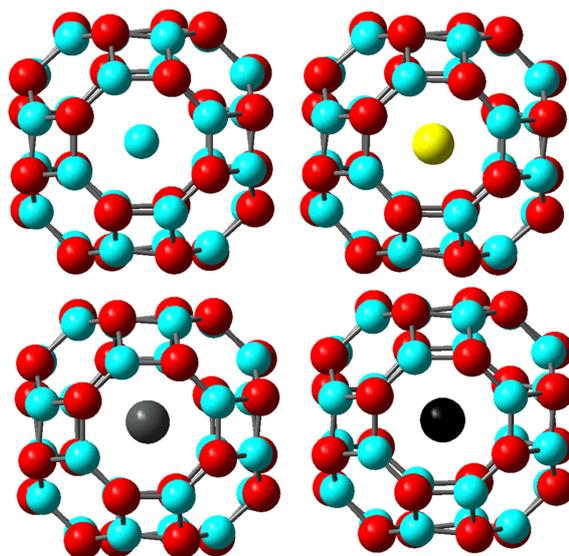


Figure 3. Optimized structure of each AEM atom encapsulated inside FLBeOC. The yellow, gray and black balls denote Mg, Ca and Sr atoms, respectively.

Table 1. Interaction energy of alkaline earth metal encapsulated FLBeOC (E_{int}), HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), Fermi level (E_{F}), HOMO-LUMO energy gap (E_{g}), work function (ϕ) and Mulliken charge ($Q_{\text{T}}|e|$) for the alkaline earth metal encapsulated FLBeOC complexes. Units are in eV

Structure	E_{int}	E_{HOMO}	E_{FL}	E_{LUMO}	E_{g}	$^{\text{a}}\Delta E_{\text{g}}(\%)$	Φ	$^{\text{b}}\Delta\phi(\%)$	$^{\text{c}}Q_{\text{T}} e $
FLBeOC	–	–10.63	–5.75	–0.87	9.76	–	4.88	–	–
Be@FLBeOC	–0.81	–8.34	–5.02	–1.70	6.64	31.96	3.32	31.96	–0.547
Mg@FLBeOC	–0.65	–6.94	–3.85	–0.75	6.19	36.57	3.10	36.47	0.367
Ca@FLBeOC	0.24	–4.71	–2.55	–0.40	4.31	55.84	2.95	39.54	–1.696
Sr@FLBeOC	0.94	–3.92	–2.04	–0.16	3.76	61.47	1.88	61.47	–0.83

^aChange of E_{g} of FLBeOC encapsulation of alkaline earth metal.

^bThe change of work function of encapsulated FLBeOC.

^c Q_{T} is defined as the Mulliken charge on the AEM atoms.

$\text{Be}_{24}\text{O}_{24}$ only one stable configuration was obtained. The optimized geometry of alkaline earth metal encapsulated FLBeOC is displayed in *Fig. 3* and energy gap (E_{g}), charge transfer, and interaction energy (E_{int}) are summarized in *Table 1*.

In contrast to Ca and Sr encapsulated FLBeOC, the result indicated that the encapsulated of Be and Mg are energetically favorable and exothermic inside the FLBeOC. The interaction energy (E_{int}) of Be@FLBeOC is -0.81 eV is more negative than that of Mg (-1.15 eV), but value of E_{int} for Ca- and Sr@FLBeOC are $+0.24$ and $+0.94$, respectively. The results indicated that encapsulation of the AEM inside the fullerene-like becomes thermodynamically more unfavorable by increasing the size of the atom.

The Mulliken charge shown in *Table 1* reveal that, the Be, Ca, and Sr atoms always perform as an acceptor whereas Mg atom performs as a donator to the FLBeOC surface. The amount of the transferred charges are -0.547 , $+0.367$, -1.696 and -0.83 corresponding to Be-, Mg-, Ca- and Sr@FLBeOC complexes, respectively. We found the average bond lengths of the endohedral fullerene-like to be longer than those of the pristine cluster. For example, in Sr@ $\text{Be}_{24}\text{O}_{24}$, the average length bond of the L_{OH} , L_{OT} and L_{HT} is about 1.51, 1.56 and 1.60 Å, respectively. This obtained result indicates that the size of the cage expands along the atomic radii.

We have explored changes in the electronic properties of the cluster with an encapsulated AEM atoms. Calculated DOS of the AEM-encapsulated cluster is shown in *Fig. 4*

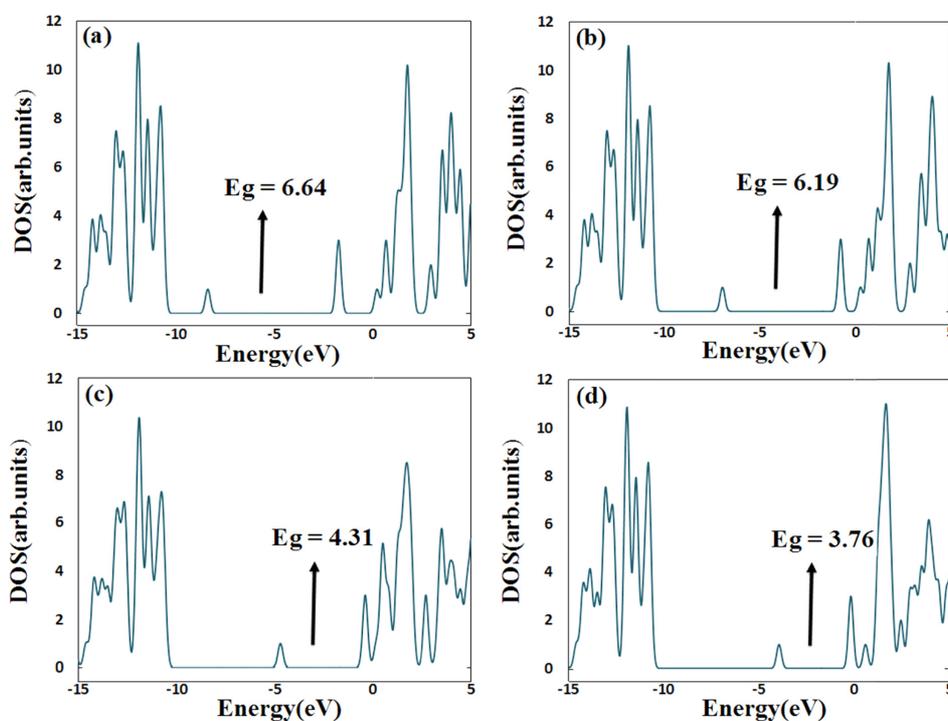


Figure 4. The DOS plots of four most stable structure for encapsulated AEM inside the FLBeOC. (a) Be@FLBeOC, (b) Mg@FLBeOC, (c) Ca@FLBeOC and (d) Sr@FLBeOC.

and the results are presented in *Table 1*, indicating that its E_g value is reduced to 6.64, 6.19, 4.31 and 3.76 eV for Be-, Mg-, Ca and Sr@Be₂₄O₂₄, respectively, compared to the pristine cluster (with $E_g = 9.76$ eV).

Table 1 shows that the Fermi level (E_{FL}) of FLBeOC significantly shifts to higher energies by encapsulated alkaline earth metal and the work function (ϕ) significantly shifts to lower energies, which is an important electronic property for evaluating field emission properties. By referring to *Table 1* the work function significantly shifts, so that ϕ of the fullerene-like decreases from 4.88 eV in bare fullerene-like to 3.32, 3.10, 2.95 and 1.88 eV for Be-, Mg-, Ca- and Sr@FLBeOC complexes, respectively. Therefore the change in the work function will change the field emission properties of the fullerene-like. It was found that the encapsulation of alkaline earth metal may facilitate the electron emission from the FLBeOC surface by reducing the work function.

Alkali Metal (AM) Encapsulation FLBeOC

The physical and chemical properties of alkali metal inside fullerene have been attractive in various fields.^{49,50} In order to investigate encapsulated behavior of Li, Na, K and Rb into the fullerene-like BeO cluster, we have located different initial encapsulation sites. To find the most stable structure of endohedral fullerene-like AM@FLBeOC, we have investigated three inner paths. Each path starts from the fullerene-like center of Be₂₄O₂₄, such as center of tetragonal, hexagonal and octagonal rings. For example in *Fig. 5*, we show the interaction energy variation with Li atom height to depth of an octagonal ring path of the FLBeOC surface. The minima of the curves correspond to the equilibrium

distance of the Li atom and FLBeOC. Interestingly, after full optimization, corresponding to each atom that encapsulated Be₂₄O₂₄, we have only obtained one stable configuration in center of BeO fullerene-like. It should be noted that the encapsulation one AM atom, only one-dimensional model for AM moving in center of Be₂₄O₂₄ cage was investigated. The optimized geometry of alkali metals encapsulated FLBeOC metallofullerenes are displayed in *Fig. 6* and energy gap (E_g), charge transfer, and interaction energy (E_{int}) are summarized in *Table 2*. In comparison with AEM encapsulation, it was found that AM encapsulation is an

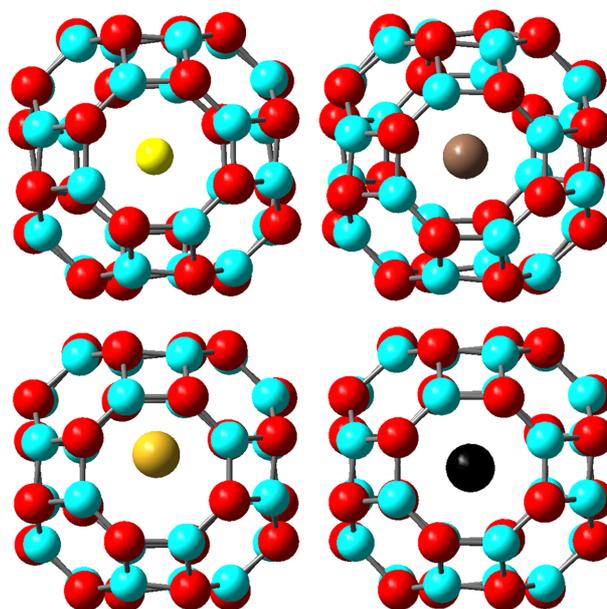


Figure 6. Optimized structure of each AM atom encapsulated inside FLBeOC. The yellow, gray, gold and black balls denote Li, Na, K and Sr atoms, respectively.

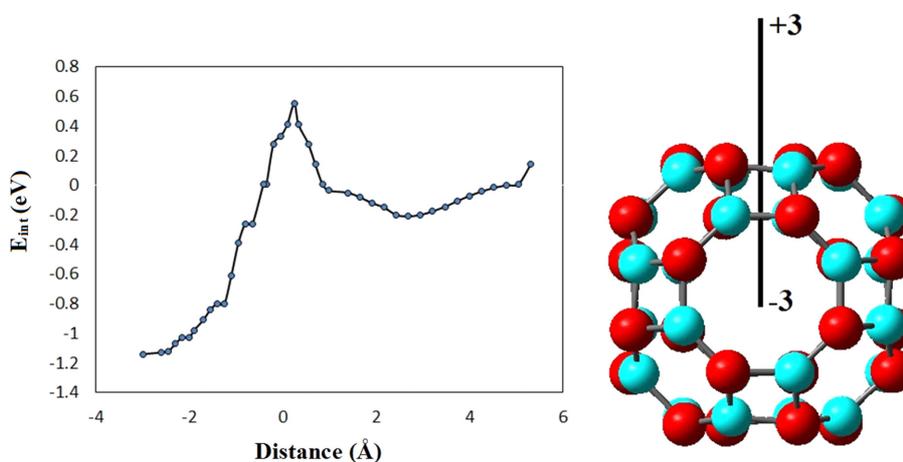


Figure 5. Interaction energy as a function of interaction distance of Li@Be₂₄O₂₄ complex, corresponding to bring in Li atom from an octagonal ring path inside the FLBeOC. +3 and -3 is refer to distance of Li atom upon and inside the octagonal ring (center of the cage) of the Be₂₄O₂₄ surface, respectively.

Table 2. Interaction energy of alkali metal encapsulated FLBeOC (E_{int}), HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), Fermi level (E_{F}), HOMO-LUMO energy gap (E_{g}), work function (ϕ) and Mulliken charge (Q_{T} |e|) for the alkali metal encapsulated FLBeOC complexes. Units are in eV

System	E_{int}	E_{HOMO}	E_{FL}	E_{LUMO}	E_{g}	$^{\text{a}}\Delta E_{\text{g}}(\%)$	ϕ	$^{\text{b}}\Delta\phi(\%)$	$^{\text{c}}Q_{\text{T}} e $
FLBeOC	–	–10.63	–5.75	–0.87	9.76	–	4.88	–	–
Li@FLBeOC	–1.15	–5.34	–3.26	–1.18	4.16	57.37	2.08	57.37	–0.903
Na@FLBeOC	–1.24	–5.35	–3.01	–0.68	4.67	52.15	2.33	52.25	–1.894
K@FLBeOC	–0.61	–3.89	–2.13	–0.38	3.51	64.03	1.75	64.13	–1.204
Rb@FLBeOC	–0.02	–3.35	–1.78	–0.21	3.14	68.82	1.57	67.82	–0.173

^aChange of E_{g} of FLBeOC encapsulation of alkali metal.

^bThe change of work function of encapsulated FLBeOC

^c Q_{T} is defined as the Mulliken charge on the AM atoms.

energetically favorable process. The result indicated that the encapsulated of alkali metal in the FLBeOC is energetically favorable and the complex is thermodynamically stable. The E_{int} of Na@FLBeOC is –1.24 eV and more negative than that of Li (–1.15 eV) and much more negative than those of K (–0.61 eV) and Rb (–0.02 eV) encapsulated FLBeOC, respectively. The following order of interaction strength of encapsulation is observed: Na > Li > K > Rb. Also, we show that our results for the interaction of AM into a $\text{Be}_{24}\text{O}_{24}$ using hybrid functional are different than those of boron cage (B_{80})⁵¹ and carbon cage (C_{60})⁵² using PW91 functional (the interaction energy, distance AM atom to nearest cage atom, and transferred charge). In Table 3, we list the main differences between our results and those of Refs. 51 and 52 for fullerene-like BeO cluster. As shown in this table, the interaction energy (E_{int}) for Li, Na and K in

$\text{Be}_{24}\text{O}_{24}$ are less negative than the previously reported Ref. 51 for B_{80} but E_{int} corresponding to Li, Na and K are more negative than previously reported Ref. 52 in C_{60} cage.

The diameter of $\text{Be}_{24}\text{O}_{24}$ expands with increasing the radius of the AM as atomic size generally increases moving down a group of the periodic table. The diameters of AM@FLBeOC complexes are found to be about 7.13, 7.13, 7.14 and 7.15 corresponding to Li-, Na-, K- and Rb- @FLBeOC, respectively.

The encapsulation process affects the structural properties of AM encapsulated FLBeOC so that the bond length of the FLBeOC is slightly changed in some cases, for example, compared with pristine fullerene-like BeO the bond length of Na@FLBeOC are increased about from 1.50 to 1.51 Å, 1.55 to 1.56 Å and 1.59 to 1.60 Å corresponding to bond length of L_{OH} , L_{OT} and L_{HT} , respectively. It should be noted that the

Table 3. List of our used method and our obtained results for an encapsulated AM@ $\text{Be}_{24}\text{O}_{24}$ cage compared to AM@ B_{80} and AM@ C_{60}

Method	Present study		Ref. 51		Ref. 52	
	DFT(M06-2X)		DFT(PW91)		DFT(B3LYP)	
Structure type	$\text{Be}_{24}\text{O}_{24}$		B_{80}		C_{60}	
$E_{\text{int}}(\text{eV})$	Li center	–1.15	Li(P)	–2.65	Li	–0.36
	–	–	Li(H)	–2.11	–	–
	–	–	Li(P)	–1.89	–	–
	Na center	–1.24	Na(H)	–1.6	Na	–0.33
	–	–	Na(P)	–2.3	–	–
	K center	–0.61	K(H)	–2.14	K	–0.33
Charge e (Mulliken)	Li center	–0.903	Li(P)	0.08	–	–
	–	–	Li(H)	0.29	–	–
	–	–	Li(P)	0.59	–	–
	Na center	–1.894	Na(H)	0.62	–	–
	–	–	Na(P)	0.78	–	–
	K center	–1.204	K(H)	0.79	–	–
d (Å)	Be- or O-AM		B-AM		C-AM	
	Li	3.4–3.65	Li(P)	2.21	Li	2.26–2.32
	–	–	Li(H)	2.29–2.55	–	–
	–	–	Li(P)	2.7	–	–
	Na	3.48–3.65	Na(H)	2.68–2.98	Na	2.47–2.53
	–	–	Na(P)	3.1	–	–
	K	3.25–3.83	K(H)	3.08–3.29	K	2.97–3.03

effect of changes in some case bonds length for Rb@FLBeOC are more than of other alkali metal encapsulated. The bigger size of Rb compared to other alkali metal atom can be a logical reason for the observed changes. The following order of change in bond length is observed: $Rb > K > Na > Li$. The encapsulation of AM, change the dipole moment of FLBeOC; from 0.009 Debye to 0.111, 0.018, 2.799 and 0.244 Debye corresponding to Li-, Na-, K- and Rb@FLBeOC, respectively. As shown in *Tables 2* and *3*, based on Mulliken charge we understand that the alkali metal atoms always perform as an acceptor in comparison to pervious reports that AM atoms perform as a donator, Ref. 51 for AM@B₈₀. The calculated charges on the alkali metal atoms are -0.903 , -1.894 , -1.204 and -0.173 |e| corresponding to most stable configuration Li-, Na-, K- and Rb@FLBeOC respectively. Also we can say that a relatively charge is transferred from the FLBeOC surface to the alkali metal atoms. In comparison to Ref. 51 the value of charge transfer of AM@C₆₀ is positive, this means a relatively charge is transferred from the AM to C₆₀ surface in *Table 3*. As shown in this table the distance of AM atom to nearest atom of cage for Be₂₄O₂₄ is larger than B₈₀ and C₆₀ cage.

In the following, the influence of the encapsulation of alkali metal on the electronic properties of the fullerene-like

has been investigated. Since the electronic conductivity of the FLBeOC can be modified by small change of energy gap (E_g), these changes of energy gap (ΔE_g) correspond to encapsulated of the AM are related to the sensitivity of the fullerene-like. The DOS plots for all encapsulation models of alkali metal inside FLBeOC have been shown in *Fig. 7*, indicating the electronic properties of the fullerene-like near the conductive level have been significantly changed compared to the pristine fullerene-like BeO. It is indicated from DOS plot of this models that its conduction level shifts to lower energies significantly, and the valence level shifts in higher energies (except in Na@FLBeOC that shift to lower energy) compared to the pristine fullerene-like BeO, therefore E_g of the encapsulation process significantly decrease as in *Table 2*. As shown in this table and *Fig. 7*, comparing DOSs of pristine and encapsulated FLBeOC indicated that the E_g decreased from 9.76 eV (the E_g of pristine FLBeOC) to 4.16, 4.67, 3.51 and 3.14 eV in the Li-, Na-, K- and Rb-encapsulated Be₂₄O₂₄, respectively. Subsequently, the encapsulation of AM inside the FLBeOC influences their DOS plots. This indicates that the electronic properties of the FLBeOC are sensitive to the AM encapsulating.

In detail, the LUMO states are mainly located on the AM atom, but the HOMO is on the FLBeOC surface. For example

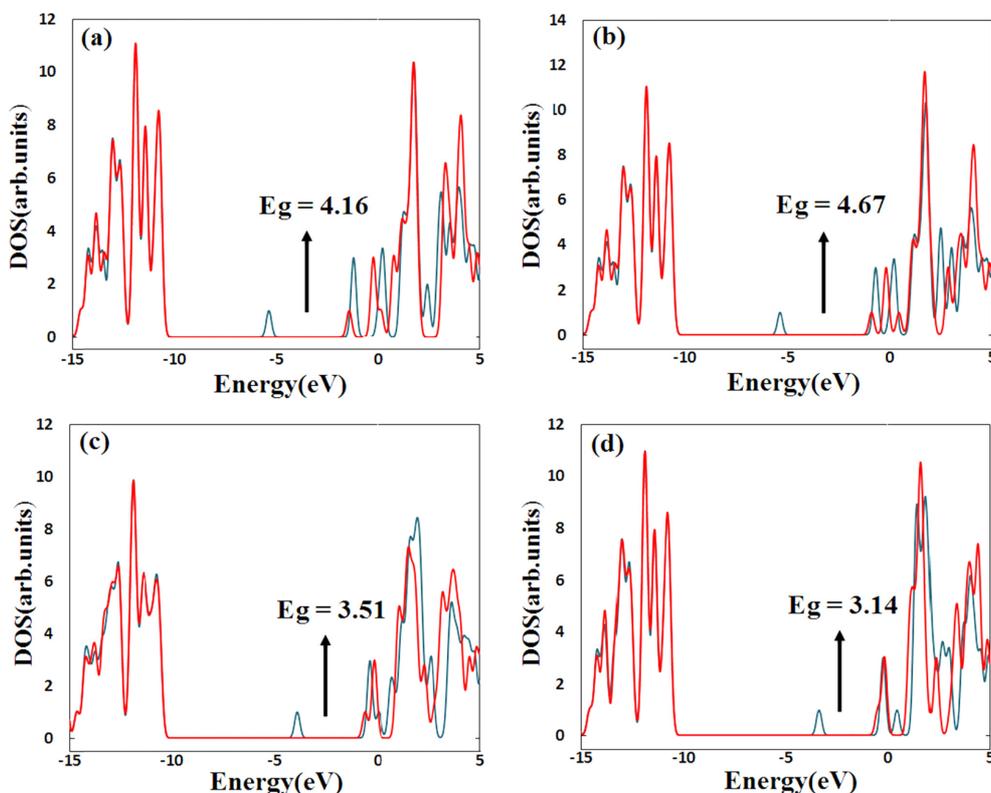


Figure 7. The DOS plots of four most stable structure for encapsulated AM inside the FLBeOC. (a) Li@FLBeOC, (b) Na@FLBeOC, (c) K@FLBeOC and (d) Rb@FLBeOC.

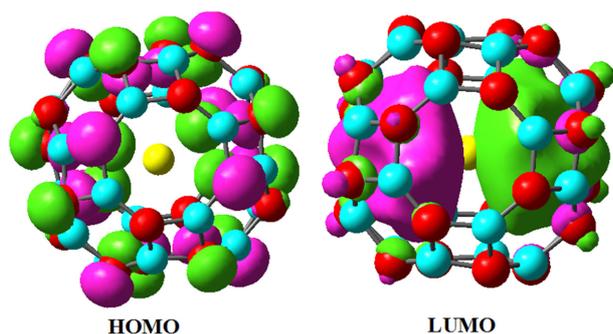


Figure 8. The HOMO and LUMO profiles of the Li@FLBeOC.

profiles of the HOMO and LUMO Li@FLBeOC represented in Fig. 8, therefore, the valence electrons of the Li atom can be mobile and give a contribution to the electronic properties of the encapsulation. It is expected that the interaction of the HOMO of the surface fullerene-like with the LUMO of Li is strong. Importantly, this change of electronic structure may be used for a wide range of next-generation components in nano-electronic device.

Nanomaterials are potential candidates to be used as electron field emission sources. The change of the Fermi level can lead to a change in the work function (ϕ), is an important electronic property for evaluating field emission properties. Work function, which is defined as energy required for electron transition from the Fermi level to vacuum level surface. The change in the work function will change the field emission properties of the fullerene-like. As it can be seen in Table 2, the Fermi level of the fullerene-like significantly increased from -5.75 eV in pristine FLBeOC to -3.26, -3.01, -2.13 and -1.78 eV correspond to Li-, Na-, K- and Rb@FLBeOC respectively, in the encapsulated state. Therefore work function decreased from 4.88 eV in free FLBeOC to 2.08, 2.33, 1.75 and 1.57 eV for Li-, Na-, K- and Rb@FLBeOC respectively. The decreased work function due to the charge transfer occurs from the fullerene-like surface to the alkali metal. The above result indicated that the encapsulation of alkali metal may facilitate the electron emission from the BeO fullerene-like.

Calculated DOS of AM and AEM encapsulated FLBeOC, indicated that HOMO and LUMO levels changed significantly (particularly AM), its E_g value is reduced compared to the pristine beryllium oxide fullerene-like. These changes of ΔE_g corresponding to encapsulated process are related to the sensitivity of the fullerene-like.

It is well known that the E_g (or band gap in bulk materials) is a major factor determining the electrical conductivity of a material and there is a classic relation between them as follows:⁵³

$$\sigma \propto \exp \frac{-E_g}{2KT} \quad (7)$$

where σ is the electrical conductivity and k is the Boltzmann's constant. According to the equation, larger E_g at a given temperature leads to smaller electrical conductivity. Therefore, the electrical conductivity of the FLBeOC changes with encapsulated AM. The considerable change of about 68.82% (Table 2) in the E_g value demonstrates the high sensitivity of the electronic properties of AM encapsulation inside the fullerene-like. So we believe that this work may be a good strategy for improving the sensitivity of beryllium oxide fullerene-like towards alkali metal, which cannot be detected by the pristine BeO clusters.

CONCLUSION

We have investigated the encapsulation of different AM and AEM atoms inside the fullerene-like of a BeO using DFT. The calculated geometric and energetic parameters such as net electron transfer and the DOS spectrums suggest that the encapsulation of AM inside the FLBeOC is exothermic and thermodynamically more favorable than AEM encapsulation. The interaction energy (E_{int}) of the alkali metal encapsulation FLBeOC is in the range of -0.02 to -1.15 eV at level of theory. On the basis of calculated changes in the HOMO/LUMO energy gap it is found that electronic properties of FLBeOC toward encapsulation of AM is more sensitive than encapsulation of AEM. The AM and AEM encapsulation decreases the work function of the fullerene-like, influencing the electron emission current from the fullerene-like surface.

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