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Optical and Electronic Properties of Al-Doped $Mg_{12}O_{12}$ Nanocluster: A Theoretical Study

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Abstract– Effects of Al doping on the structural, optical, and electronic properties of $Mg_{12}O_{12}$ nanocluster have been investigated using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations. It is found that for all stable structures, the doped nanocluster with five Al atoms has a larger binding energy of –5.22 and –5.06 eV evaluated by M06-2X and B97D functional, respectively. Both M06-2X and B97D functional exhibited that the Al substituted at the Mg-site can alter the energy gap of the nanocluster in comparison with unstable O sites. With substituting four Al atoms at the Mg sites of the nanocluster, the changes in the energy gap is significantly large than other states. More details on the dopant effects, charge population and electronic structure evolution with the variation of the Al concentration of doping are discussed in the context.

Keywords: $Mg_{12}O_{12}$, doping, DFT, optical properties, electronic structure
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INTRODUCTION

After the discovery of carbon nanotubes created a revolution in science and technology as the scientists were interested in the properties of nanoscale materials because of their extraordinary properties and researches many attempts were made to investigate the inorganic nanostructures [1–3]. Today fullerenesare-considered in nanotechnology because of specific features in electronic devices, imaging materials, magnetic recording and etc. [4–9]. Thereafter, many scientists are interested in these types of clusters and it is the main topic of wide researchers. Among the various nanostructures, II–VI semiconducting has shown special attention of scientists. In this case, the MgO nanostructures are promising materials for practical usages as the reports showed that MgO nanostructures are convenient for hydrogen storage [10–12]. Since researchers revealed that doped with atoms of net foreign clusters improve their properties and expanding their applications, after checking the pure clusters study of doped clusters was a fascinating subject for physicists and chemists [13, 14]. Liu and co-workers studied the electronic properties of MgO doped with group III, IV, and V elements. They found that with substituting O in MgO, the system shows half-metallic ferromagnetic properties [15]. Kakemam and Peyghan have been theoretically studied the electronic, energetic, and structural properties of $Mg_{12}O_{12}$ nanoclusters [16]. They have been shown the influence of C and Si atoms on the electronic, energetic, and structural properties of $Mg_{12}O_{12}$ nanocluster. It has been found that substitution of each Mg atoms of the nanocluster through C or Si atom is favorable than the substitution of O atom [16]. Shakerzdeh and coworkers [17] were investigated the effect of alkali metals on the electronic and optical properties of $Be_{12}O_{12}$ and $Mg_{12}O_{12}$ nanoclusters. Since metal oxides are widely used as the sensor many scientists were concerned. Kana et al. [18] have studied quantum mechanical modeling of electronic excitations within MgO as a prototypical metal oxide. Eventually, we decided to perform a detailed theoretical study on doping of Al on the $Mg_{12}O_{12}$ nanocluster through density functional theory calculations.

THEORETICAL

Various form structures of Al-doped $Mg_{11}O_{12}$ were simulated and optimized by substituting one or more Al atoms for magnesium atoms of adsorbent using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations. In our forms, a study over geometry optimizations, energy calculations, and density of states analysis was

Table 1. Calculated the bond length of pure and Al-doped $Mg_{12}O_{12}$ nano-cages on different sites

Property	M06						B97D					
	$X_{Mg-O(1)}$	$X_{Al-O(1)}$	$Y_{Al-O(1)}$	$Z_{Al-O(5)}$	$E_{Al-O(7)}$	$F_{Al-O(6)}$	$X_{Mg-O(1)}$	$X_{Al-O(1)}$	$Y_{Al-O(1)}$	$Z_{Al-O(5)}$	$E_{Al-O(7)}$	$F_{Al-O(6)}$
$Mg_{12}O_{12}$	1.939	–	–	–	–	–	1.971	–	–	–	–	–
$Mg_{11}Al\ O_{12}$	1.952	1.826	–	–	–	–	1.982	1.864	–	–	–	–
$Mg_{10}Al–AlO_{12}$	1.944	1.741	2.102	–	–	–	1.970	1.884	1.876	–	–	–
$Mg_{10}Al_2O_{12}$	2.011	–	1.774	1.743	–	–	2.015	–	1.821	1.769	–	–
$Mg_9Al_3O_{12}$	1.944	–	1.840	1.809	1.741	–	1.971	1.866	–	1.817	1.788	–
$Mg_8Al_4O_{12}$	1.932	–	1.899	1.736	1.733	1.894	1.969	–	1.902	1.767	1.760	1.898
$Mg_7Al_5O_{12}$	1.946	1.826	–	1.781	1.761	2.001	1.982	–	1.856	1.807	1.781	2.001

carried out upon the pristine and Al-doped $Mg_{11}O_{12}$ using unrestricted M06-2X functional [19, 20] and CC-PVDZ basis set [21] as implemented in GAMESS suite of the program [22]. The B97Dwas chosen for a better description of dispersion interactions in the absorption systems [23]. Gauss Sum program has been used to obtain the DOS results [24]. The M06-2X and B97D have been previously demonstrated being reliable and commonly used functions to study of different nanostructures. These levels of calculations are a fascinating approach which has been commonly used for structures. Doping energy (E_{dop}) of the Al atom was calculated according to the following equation:

$$E_{dop} = E(Mg_{11}XO_{12}) + E(Mg) - E(Mg_{12}O_{12}) - E(X),$$

where $E(Mg_{11}XO_{12})$ and $E(Mg_{12}O_{12})$ are the total energies of the doped and pure $Mg_{12}O_{12}$ nano-clusters, while E(Mg) and E(X) are the total energies of an isolated Mg and Al atom, respectively. The negative value of E_{doped} indicates an exothermic reaction.

RESULTS AND DISCUSSION

Here, we investigated the influence of Al doping on the electronic and optical properties of the $Mg_{12}O_{12}$ cluster using two functional, M06-2X and B97D in comparison with free $Mg_{12}O_{12}$ nanocluster. Afterwards, we have been made six additional models by completely randomly altering the positions of Al and Mg atoms in the adsorbent. It is presented in Table 1 and Fig. 1, the length of Mg-O bond of the free model increases from 1.939 Å to 1.952 ($Mg_{11}AlO_{12}$), 2.011 ($Mg_{10}Al_2O_{12}$), 1.944 ($Mg_9Al_3O_{12}$), and 1.946 Å ($Mg_7Al_5O_{12}$) by M06 functional, while the length of Mg–O bond of the free model raises from 1.971 Å to 1.982 ($Mg_{11}AlO_{12}$), 2.015 ($Mg_{10}Al_2O_{12}$), 1.971 ($Mg_9Al_3O_{12}$), and 1.982 Å ($Mg_7Al_5O_{12}$) by B97D functional, respectively, which are in agreement with previous reports [25]. Kakemamand Peyghan [16] have been found that the length of Mg–O and Si–O bonds for pure and Si-doped $Mg_{12}O_{12}$nanoclusters are about 1.92 and 1.78 Å, respectively. For $Mg_{12}O_{12}$ doped with the Al atoms, the gained binding energies are strongly exothermic with the values of –1.26 ($Mg_{11}AlO_{12}$), –2.62 ($Mg_{10}Al_2O_{12}$), –3.73 ($Mg_9Al_3O_{12}$), –4.23 ($Mg_8Al_4O_{12}$), and –5.06 eV ($Mg_7Al_5O_{12}$) by B97D functional (see Table 2). In contrast with B97D functional, the values of binding energy for $Mg_{11}AlO_{12}$, $Mg_{10}Al_2O_{12}$, $Mg_9Al_3O_{12}$, $Mg_8Al_4O_{12}$, and $Mg_7Al_5O_{12}$ nanoclusters are found to be –1.18, –2.01, –2.06, –3.03, –3.44, and –5.22 eV by M06 functional, respectively. Thus, the Al atom can lead to a local structural deformation at the doping site. Morkovite and co-workers have shown that the absorption energy of the Mn,Co, and Fe atoms upon the surface of MgO (100) is –0.596, –0.802, and –0.805 eV by GGA method, respectively [26]. Regarding the Javan et al., it is observed that the maximum of the binding energy for $Mg_{11}(TM)O_{12}$ nanoclusters (TM: Mn, Fe, Co, and Ni atoms) are about –4.18, –4.24, –4.33, and –4.27 eV, respectively [25].

As it can be clearly seen from Fig. S1 in the Supporting Information, the values of dipole moment (DM) for all forms are calculated.For the stable Al-doped $Mg_{12}O_{12}$nanocluster models, the calculated dipole moment values are in the range of 2.07–6.18 Debye. Clearly, in the most stable state, the doping of Al atom in $Mg_{12}O_{12}$ nanocluster leads to increase of dipole moment from zero Debye in the free model to 4.66 and 5.88 Debye in the $Mg_7Al_5O_{12}$ complex by B97D and M06-2X functional, respectively. Table 2 represents that the changes in the electronic properties of an adsorbent by Al doping in different positions. It is interesting that the results obtained in Fig. 1 indicates that the electronic structures of $Mg_{12}O_{12}$ nanocluster with the tetrahedral (T_h) symmetry are rather robust against doping level with Al atoms; there is a Jahn-Teller effect because of the geometrical distortion of the nanocluster. The NBO analysis represents that the electron configurations for Alatom ($Mg_{11}AlO_{12}$) after the doping process are altered from [Ne] $3S^{1.0}$ $3P^{0.02}$ to [Ne] $3S^{0.63}3P^{0.52}$. Hence, we can expect our complexes to be sagely closed to other papers [27, 28]. As shown