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In_4Mg_3 in In_xMg_3 ($x = 1 - 6$) series: a magic unit for future smart materials

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Systematic investigation on the stability and electronic properties of a series of bimetallic (semiconductor-alkaline earth) clusters, viz., In_xMg_3 ($x = 1-6$) is performed, in the search for exceptionally and/or unusually stable motifs. A very popular hybrid exchange-correlation functional, B3LYP as proposed by A. D. Becke is employed for this purpose under the density functional formalism. The magic stability among the concerned clusters is explained using the jellium model. It is evident from the present study that the magic stability of In_4Mg_3 cluster arises due to the jellium shell closure and found as a potential building block for future novel semiconductor materials.

Keywords: Magic clusters, jellium model, density functional theory, smart materials.

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1. Introduction

As a consequence of the discovery of fullerene [1], atomic and molecular clusters have gained immense attention as the potential candidates for designing novel nanomaterials [2–4]. The most important fact is that atomic clusters of sub-nano or nano-scale dimensions exhibits drastic differences in the physicochemical properties compared to their bulk counterparts, due to the effect of quantum confinement. This important behavior of nano-scale materials are found to be very useful in various technical applications over the last two decades or so [1–7].

In order to overcome the usual meta-stable nature of many clusters, one main focus of researchers is to search for the clusters with unusual or exceptional stability and/or useful physicochemical properties. The jellium is a quantum mechanical model of interacting electrons within an infinite volume of space and neutralized with an artificially assumed uniformly distributed background positive charge [8]. The jellium is usually treated within the density functional theory (DFT) [9, 10], since at zeroth temperature the properties of a jellium depend solely on electron density (ρ) [8]. Through an experimental mass spectra of a series of sodium clusters, W. D. Night et al. [11] have noticed that sodium clusters with a certain total number of valence electrons, viz., 2, 8, 18, 20, 34, 40, 52, ... etc. shows exceptional stability compared to their neighbors. Such exceptionally stable clusters are named as magic clusters, and based on the jellium model as mentioned above and similar to the electronic shell structure of atom, they have proposed a new cluster valence shell structure in terms of the total valence electrons of the magic clusters as $1S^2 1P^6 1D^{10} 2S^2 1F^{14} 2P^6$ .... Such cluster shell structure essentially represents the total valence electrons as observed for magic clusters with shell closure as $2(1S^2)$, $8(1S^2 1P^6)$, $18(1S^2 1P^6 1D^{10})$, $20(1S^2 1P^6 1D^{10} 2S^2)$, $34(1S^2 1P^6 1D^{10} 2S^2 1F^{14})$ etc. The exceptionally stable cluster motifs may have potency for utilizing them as the building blocks for designing novel cluster assembled materials.

The purpose of the present work is to perform a detailed study on the geometries, electronic properties as well as to search for any unusual and/or exceptionally stable cluster building motifs from the In_xMg_3 ($x = 1 - 6$) cluster series. The electronic properties include energy gain in adding an indium atom (ΔE_{In}) to the previous sizes, HOMO-LUMO energy gap (*HLG*), ionization potential (*I.P.*), chemical hardness (η) etc.

2. Theory and computation

The energy gain (ΔE_{In}) in forming In_xMg_3 clusters by adding an indium atom to the previous $In_{x-1}Mg_3$ ($x = 1 - 6$) size is given as:

$$\Delta E_{\mathrm{In}} = E\left(\mathrm{In}\right) + E\left(\mathrm{In}_{x-1}\mathrm{Mg}_3\right) - E\left(\mathrm{In}_x\mathrm{Mg}_3\right), \tag{1}$$

where $E(\mathrm{In}_x\mathrm{Mg}_3)$, $E(\mathrm{In}_{x-1}\mathrm{Mg}_3)$ and $E(\mathrm{In})$ are the total energies of the In_xMg_3, $In_{x-1}Mg_3$ clusters and of the In atom, respectively.

Using Koopmans' finite difference approximation, the ionization potential (*IP*) and electron affinity (*EA*) can be expressed in terms of the highest occupied (ϵ_{HOMO}) and the lowest unoccupied (ϵ_{LUMO}) molecular orbital energies as:

$$IP \approx -\epsilon_{HOMO}; \qquad EA \approx -\epsilon_{LUMO}. \tag{2}$$

The chemical hardness can be expressed in terms of ϵ_{HOMO} and ϵ_{LUMO} as follows:

$$\eta \approx \frac{IP - EA}{2} \approx \frac{\epsilon_{LUMO} - \epsilon_{HOMO}}{2}. \tag{3}$$

The theoretical investigations are carried out within the density functional theory (DFT) framework [9, 10]. A molecular orbital approach, using a linear combination of atomic orbitals, is applied to probe the electronic structure. The actual DFT based calculations are performed using GAUSSIAN 09 [12] program. We have used B3LYP exchange-correlation functional [13] and LANL2DZ basis sets [14] for our calculations. A large number of initial guesses in every possible way is considered for each of the In_xMg_3 ($x = 1 - 6$) clusters to predict their ground state structures. The geometries of optimized clusters are drawn with CHEMCRAFT [15] visualization software.

3. Results and discussion

The ground state structures of In_xMg_3 ($x = 1 - 6$) clusters along with the geometrical bond lengths and point groups is represented in Fig. 1. The point group of various structures is considered within the tolerance limit of 0.1 Å. The profile of energy gain (ΔE_{In}) in forming each clusters by adding one indium atom to an existing $In_{x-1}Mg_3$ ($x = 1 - 6$) cluster is provided in Fig. 2.

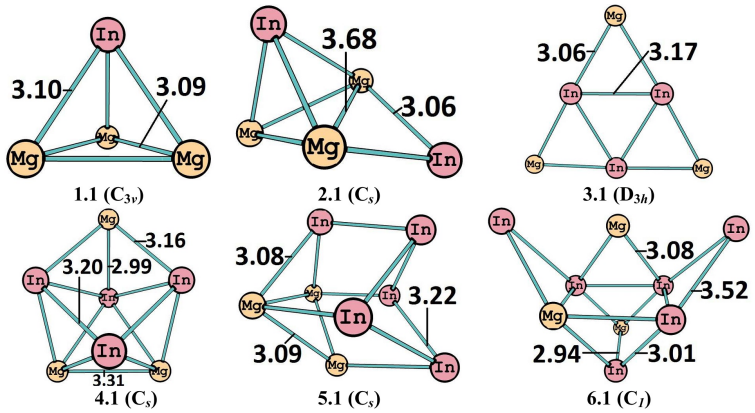

FIG. 1. Ground state structures and associated point groups of In_xMg_3 ($x = 1 - 6$) clusters. Isomer $x.n$ ($x = 1 - 6$) represents the clusters with x boron atoms in its lowest energy state ($n = 1$). The bold numbers on the cluster images show a few representative bond distances between In–In, Mg–Mg and In–Mg atoms in Angstroms (Å)

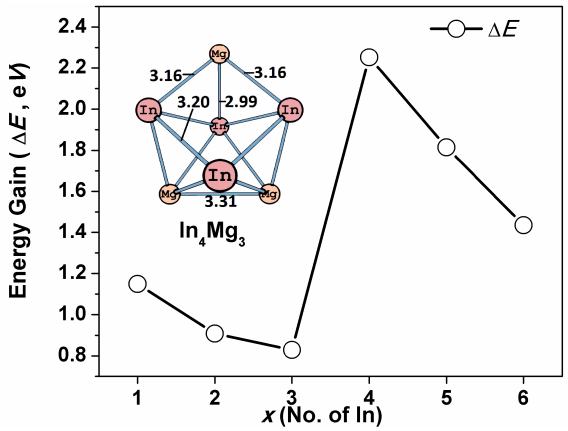

FIG. 2. Energy gain (ΔE) of In_xMg_3 clusters, in adding an indium atom to an existing $In_{x-1}Mg_3$ ($x = 1-6$) cluster. The bold numbers on the cluster image show few representative bond distances between In–In, Mg–Mg and In–Mg atoms in Angstroms (Å)

It can be noticed that, In_4Mg_3 cluster has very high energy gain (2.25 eV) compared to its neighboring clusters, implying its exceptional stability in the considered series. The stability of In_4Mg_3 is expected from the jellium framework since the number of valence electrons of the system is 18, which is a magic number with cluster electronic shell closure as $1S^21P^61D^{10}$. Table 1 provides the energy gain (ΔE_{In}), HOMO-LUMO energy gap (HLG), ionization potential (IP), electron affinity (EA) and chemical hardness (η) of the In_xMg_3 ($x = 1 - 6$) clusters. The maximum values of ΔE_{In} (2.25 eV) for In_4Mg_3 cluster justifies itself as the most stable motif in the series. The stability of the In_4Mg_3 cluster is further confirmed by its large I.P. (4.31 eV) value.

TABLE 1. Energy gain in adding an In atom (ΔE) to an existing $In_{x-1}Mg_3$ ($x = 1-6$), HOMO-LUMO energy gap (*HLG*), ionization potential (*IP*), electron affinity (*EA*) and chemical hardness (η) of the In_xMg_3 ($x = 1 - 6$) clusters

X	***ΔE (eV)***	***HLG (eV)***	***IP (eV)***	***EA (eV)***	***η (eV)***
1	1.15	2.20	4.36	2.16	1.10
2	0.91	1.23	3.58	2.35	0.62
3	0.82	0.85	3.71	2.86	0.42
4	2.25	1.19	4.31	3.12	0.60
5	1.82	1.95	4.34	2.39	0.98
6	1.44	1.55	4.26	2.71	0.77

In summary, In_4Mg_3 cluster is identified as a new magic cluster in the family of bimetallic magic clusters [16–18]. The possibility of utilizing In_4Mg_3 cluster as a potential building block for future cluster assembled materials by linking them with suitable inorganic/organic linkers is currently being investigated in our laboratory.

4. Conclusions

A detail theoretical study was performed in the search for exceptionally stable or magic clusters in the In_xMg_3 ($x = 1 - 6$) series. In_4Mg_3 shows magic stability with the effect of jellium shell closure. The significant energy gain, HOMO-LUMO energy gap (*HLG*), ionization potential, chemical hardness and electron affinity explain the origin of the extraordinary stability of In_4Mg_3 motif and imply its suitability to be considered as a building motif for novel inorganic nanomaterials. Also, the HLG value for In_4Mg_3 as 1.19 eV implies an initial classification for its suitability for application towards the design of novel semiconductor materials.

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