

## Structures, stabilities and electronic properties of $M\text{Sn}_{10}$ ( $M=\text{Li}, \text{Be}, \text{B}, \text{Ca}$ )

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**Abstract.** The effect of impurity atoms on structures, stabilities and electronic properties of  $M\text{Sn}_{10}$  ( $M= \text{Li}, \text{Be}, \text{B}$  and  $\text{Ca}$ ) clusters have been investigated using the density functional theory based B3LYP method with cc-pVTZ(-PP) basis set. The results show that the location of the impurity atom depends on the interactions of impurity atoms with the host cluster and the size of the impurity atom itself. The stability has been analyzed based on average binding energy, vertical ionization potential, vertical electron affinity, HOMO - LUMO energy gap and embedding energy. Several clusters, such as  $\text{BeSn}_{10}$ ,  $\text{Sn}_{10}$  and  $\text{Sn}_{10}^{(2-)}$  with enhanced stability have been identified. The stability of  $\text{Sn}_{10}(\text{C}_{3v})$  can be rationalized using the jellium shell model. Molecular orbital analyses reveal that the enhanced stability of  $\text{BeSn}_{10}$  and  $\text{Sn}_{10}^{(2-)} (\text{D}_{4d})$  with 42 valence electrons may arise from a crystal-field splitting of the 1G shell and from the closed-shell nature of the  $\pi$  subsystem, which is subjected to the  $2(N_{\pi}+1)^2$  rule with  $N_{\pi}=1$ . Both  $\text{BeSn}_{10}$  and  $\text{Sn}_{10}^{(2-)}$  clusters can be considered to be aromaticity with  $8\pi$  electrons, further confirmed by the large nucleus-independent chemical shift values.

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**Key words:** tin cluster, stability, molecular orbital, aromaticity, nucleus-independent chemical shift

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## 1 Introduction

Since the discovery and macroscopic production[1,2] of fullerenes, the questing for novel highly symmetrical and chemically inert cluster is a focus in current research[3-6], which should be very promising potential building blocks for designing new cluster-assembled nanostructured materials. Symmetric binary clusters could be the ideal building blocks

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for these advanced materials, since their unique physicochemical properties can be manipulated nearly at will by altering size, shape, and composition[5,7]. Recently, a larger number of experimental and theoretical investigations have been performed on metal-encapsulated E clusters (E= Ge, Sn, and Pb)[4-14]. For examples, the mass spectral characterization of gas-phase Al-doped  $Pb_n^+$  clusters was reported by Neukermans *et al.*[4], and found considerably enhanced stability of  $AlPb_{10}^+$ . Geometry optimization at the B3LYP/LanL2DZ level of density functional theory reveals that  $AlPb_{10}^+$  is a bicapped tetragonal antiprism structure with  $D_{4d}$  symmetry, which the Al atom is encapsulated in a highly coordinated central position. The high stability for  $AlPb_{10}^+$ , which has 21 delocalized orbitals containing 42 valence electrons is attributed to the close-packed geometrical structure and the crystal-field splitting of the high angular momentum spherical molecular orbital levels according to the structural symmetry of the cluster[15,16]. Then Chen *et al.*[6] calculated the electronic structures and stability of cationic  $AlPb_{10}^+$  cluster. The enhanced stability of  $AlPb_{10}^+$  may arise from the closed-shell nature of the  $\pi$  subsystem according to the electron counting rule, namely, the  $2(N_\pi + 1)^2$  rule[17] with  $N_\pi = 1$ , which describes the spherical aromaticity. The large nucleus-independent chemical shift (NICS) values[18] indeed demonstrate the high stability of the cationic  $AlPb_{10}^+$  cluster. Subsequently, Bhattacharyya *et al.* further demonstrated the extraordinary high stability of  $AlPb_{10}^+$  cluster by mass-selected photodissociation study[19].

A few years ago, Lievens and coworkers[10] demonstrated experimentally that the  $ZnSn_{10}$  with  $D_{4d}$  symmetry system is a species with enhanced stability; even it is less abundant than the  $ZnSn_{12}$  in the experimental mass spectra. Subsequently,  $ZnSn_{10}$  cluster has been calculated that possessing 42 valence electrons  $ZnSn_{10}$  cluster was assigned to be magic cluster with a spherically aromatic character that satisfies the electron counting rule of  $2(N_\pi + 1)^2$ , namely, containing 8 valence  $\pi$ -electrons with  $N_\pi = 1$ [11]. The enhanced stability of the  $ZnSn_{10}$  can also be rationalized by its closed crystal field splitting shell. Recently, coinage metal-encapsulated 10-atom E clusters[12] (E= Ge, Sn, and Pb) were investigated by Tai *et al.*, and found that the global minima with  $D_{4d}$  structure anions, which possess 42 valence electrons, turned out to be magic clusters. The enhanced stability of these magic clusters can be rationalized by the spherical aromaticity[17]. Then, they sequentially investigated  $Ge_{10}$  and  $Ge_{10}^{2-}$  clusters[13] and found they also possessed high stabilities. The investigation reveals that each Ge atom is expected to contribute its four valence electrons to the electron shell configuration, and the result of  $Ge_{10}$  contains 40 valence electrons, which is consistent with the electron shell configuration of 40 electrons of jellium shell model (JSM)[20]. Adding two excess electrons into the neutral  $Ge_{10}$  forming  $Ge_{10}^{2-}$  cluster, leads to an unstable system with open electronic shell configuration. However, due to a distortion to  $D_{4d}$  symmetry, the 1G-subshell of  $Ge_{10}^{2-}$  is splitting into 2P-subshell which results in a very pronounced energy gap (2.92 eV) at the 42 electron occupancy. They both also can consistently be rationalized by using the spherical aromaticity.

Although a number of experimental and theoretical studies have reported the geometric and electronic properties of small doped Sn clusters, most of these works have