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Impurity-doped Si_{10} cluster: Understanding the structural and electronic properties from first-principles calculations

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Structural and electronic properties of metal-doped silicon clusters (MSi_{10}, M=Li, Be, B, C, Na, Mg, Al, and Si) have been investigated via *ab initio* molecular dynamics simulation under the formalism of the density functional theory. The exchange-correlation energy has been calculated using the generalized gradient approximation method. Several stable isomers of MSi_{10} clusters have been identified based on different initial configurations and their relative stabilities have been analyzed. From the results it is revealed that the location of the impurity atom depends on the nature of interaction between the impurity atom and the host cluster and the size of the impurty atom. Whereas Be and B atoms form stable isomers, the impurity atom being placed at the center of the bicapped tetragonal antiprism structure of the Si_{10} cluster, all other elements diffuse outside the cage of Si_{10} cluster. Further, to understand the stability and the chemical bonding, the LCAO-MO based all electron calculations have been carried out for the lowest energy isomers using the hybrid B3LYP energy functional. Based on the interaction energy of the M atoms with Si_{10} clusters it is found that *p*-*p* interaction dominates over the *s*-*p* interaction and smaller size atoms interact more strongly. Based on the binding energy, the relative stability of MSi_{10} clusters is found to follow the order of $CSi_{10} > BSi_{10} > BeSi_{10} > Si_{11} > AlSi_{10} > LiSi_{10} > NaSi_{10} > MgSi_{10}$, leading one to infer that while the substitution of C, B and Be enhances the stability of the Si_{11} cluster, others have an opposite effect. The extra stability of the $BeSi_{10}$ clusters is due to its encapsulated close packed structure and large energy gap between the HOMO and LUMO energy levels.

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INTRODUCTION

The study of silicon is important due to its technological relevance towards the development of nanoelectronics, which gives an extra impetus to understand the properties of silicon with its miniaturization. Hence, Si clusters have been studied most extensively using both theoretical and experimental techniques.[1–26] The recent experimental evidence of the formation of stable metal-encapsulating silicon cage cluster ions for MSi_n (with M=Hf, Ta, W, Re, Ir, etc., and n=14, 13, 12, 11, 9, respectively) by Hiura *et al.*[27] has revived the interest to understand the interactions of metal atoms with Si clusters. This finding aroused significant interest to search for the cage-like Si clusters stabilized by metal atom incorporation. Stimulated by the experimental findings, several computational investigations have been performed for metal-doped silicon clusters.[28–36] Very recently, Kumar and Kawazoe[37,38] reported several types of metal-encapsulating caged structures with high stability for a series of MSi_n clusters for n=14–17, M=Cr, Mo, W, Fe, Ru, Os, Ti, Zr, Hf. Following this work, a number of cage-like structures for Si cluster have been reported by other workers.[39] From the above studies it is clear that the nature of metal atoms and their interaction with Si plays an important role to modify the bonding and thereby structure of the host cluster.

Although several reports are available on the interaction of TM atom with Si clusters, similar investigations with simple metal atoms are very few. Kishi *et al.*[40] carried out a combined experimental and theoretical study of $NaSi_n$($n<7$), and found that the Na atom acts as an electron donor to the Si_n framework and the most stable isomer of $NaSi_n$ retains the framework of the corresponding Si_n cluster nearly unchanged upon the adsorption of Na. In our previous work[41] we have systematically investigated the geometry and electronic structure of Al atom substituted Si clusters and it is found that the ground state geometries of the $AlSi_{n-1}$ clusters adopt the structure of Si_n clusters where the Al atom is replacing one of the Si atoms with small local distortions. However, significant differences have been observed in their electronic structure and fragmentation behavior. Recently Kumar *et al.*[42] have carried out theoretical investigations on divalent-metal (M)-atom-doped X_N (X=Si, Ge, and Sn, N=8–12 and 14, M=Be, Mg, Ca, Zn, Cd,). It has been found that in the presence of these impurity atoms the ten atom magic clusters of Gr. IV elements become more symmetric. It can be noted that all these divalent atoms have filled electronic shells in the outermost orbital and therefore interactions are likely to be similar except for their size effects. In another work Kumar *et al.*[43] have shown that ten atom clusters of Gr. IV elements can further be stabilized by doping with transition metal atoms like Ni or Pt atoms. Few works have been reported for the interactions of the transition metal atoms with magic Si_{10} clusters; however interactions with simple metal atoms having *s* and *p* electrons in the outermost orbitals are scarce. In previous experimental[44] and theoretical studies[45] it has been observed that the stability of the Si_{11} cluster can be improved over the Si_{10} cluster by charging on it. In a recent experimental work metal-encapsulated superatom clusters of $AlPb_{10}^+$ and $AlPb_{12}^+$ clusters have been reported[46] Motivated by these results, in the present work systematic theoretical investigations have been carried out for the geometries and energetics of several isomeric structures of the MSi_{10} clusters and the results have been analyzed to understand the effect of different type (size and valence electron) impurity atoms with varying number of valence electrons with Si$_{10}$ cluster. We have chosen the impurity M atoms, which are lighter than Si and having no *d* orbitals as a core so that the interactions of the valence electrons would primarily govern by the *s-p* or *p-p* interactions. The reason for choosing Si$_{10}$ as host cluster is due to its higher stability and larger size to accommodate one impurity atom inside.

COMPUTATIONAL DETAILS

For Si$_{10}$ and Si$_{11}$ clusters, we have examined a number of possible isomeric structures as predicted earlier by several groups based on Hartree–Fock and density functional theory.[15–26] *Ab initio* molecular dynamics simulations were performed using the ultrasoft pseudopotential approach as implemented in VASP.[47] The geometries were optimized under the spin-polarized density functional theory formalism using the generalized gradient approximation to describe the exchange-correlation functional.[48] A simple cubic cell of 15 Å dimension with the Γ point for the Brillouin zone integration was considered for these calculations. The geometries are considered to be converged when the force on each ion becomes 0.01 eV/Å or less.

Further, to verify the results obtained under the plane wave pseudo-potential (PWPP) approach an all electron LCAO-MO based method has been employed to reoptimize the lowest energy isomers obtained using the PWPP method. For this purpose a standard split-valence basis set with polarization functions $(6\text{-}31G(d))$ was used at the B3LYP level[49] as implemented in the GAMESS software.[50]

RESULTS AND DISCUSSION

To begin with, the ground state geometries of Si$_{10}$ and Si$_{11}$ clusters have been evaluated with a view to have better understanding of the isomeric structures of the *M* atom doped Si$_{10}$ clusters and the effect of the interactions of different *M* elements on the stability of the host Si$_{10}$ cluster. The geometry optimization of the Si$_{10}$ cluster was carried out for various isomeric structures. It is found that the lowest energy isomer of the Si$_{10}$ cluster forms tetracap trigonal prism (TTP) structural framework. This is in agreement with previously reported results using different theoretical techniques. The second low-lying isomer, a tetracapped octahedron, is significantly higher in energy (1.34 eV) as compared to the TTP isomer. For the Si$_{11}$ cluster, different low-energy isomers have been obtained, which are nearly degenerate as shown in Fig. 1. The tricapped (adjacent positions) tetragonal antiprism with C$_{2v}$ symmetry shows the lowest energy structure. Another isomer, which is degenerate with it, also forms a tricapped tetragonal antiprism with different capping site. The stability of Si$_{10}$ and Si$_{11}$ clusters have been compared with respect to their average binding energy (*total binding energy per atom*), which suggests that the stability decreases from 3.79 to 3.73 eV by the addition of one more Si atom to the Si$_{10}$ cluster.

ISOMERIC STRUCTURES OF THE *M*Si$_{10}$ (*M*=Li, Na, Be, Mg, B, Al, AND C) CLUSTERS

The interaction of an impurity atom with a homoatomic cluster can lead to three different possibilities, viz. (a) the impurity atom can occupy the center of the cage formed by the host cluster (*endohedral*), (b) the impurity atom can adsorb on the surface of the host cluster (*exohedral*) and (c) the impurity atom can replace one atom from the network of the host cluster (*substitutional*). Based on this we have optimized 12 isomeric structures of each *M*Si$_{10}$ clusters (total $7 \times 12 = 84$) to explore the lowest energy structures of the *M*Si$_{10}$ clusters. In Fig. 2 we have shown a few representative low-lying isomeric structures of the *M*Si$_{10}$ cluster.

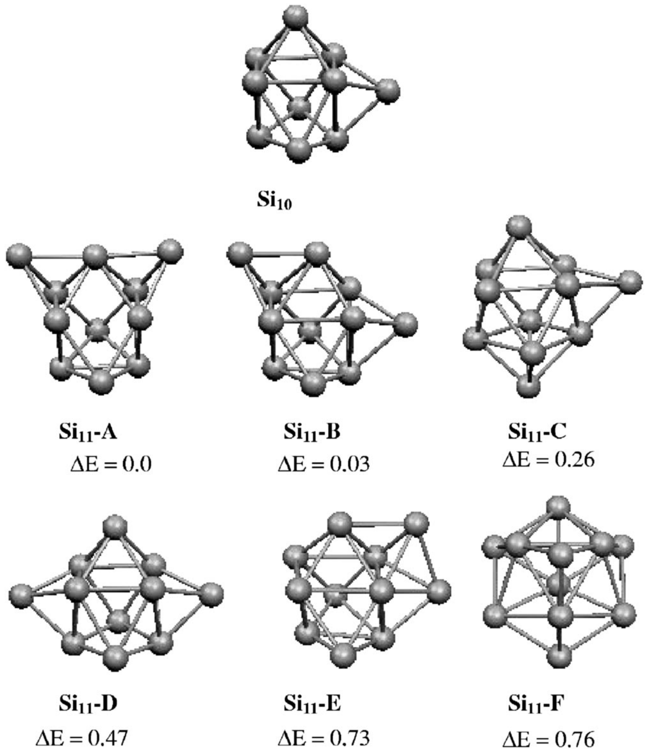

FIG. 1. The ground state geometries of the Si$_{10}$ and a few low-lying isomers of the Si$_{11}$ clusters obtained by using the *ab initio* molecular dynamics simulation umder the GGA exchange-correlation energy functional. The relative stabilities of the Si$_{11}$ isomers represent the differences in the total energies (eV) as compared to the lowest energy isomer (Si$_{11}$–A).

The impurity atoms Li and Na have one electron in their outermost *s* orbital. Figure 2 shows a few low-lying isomers of Li and Na atom doped Si$_{10}$ cluster. Interestingly we notice that the relative stability of the lowest energy isomers has changed for these two impurity atoms of different sizes. Whereas in the case of Li, a fourfold coordination site is more preferable but for Na a threefold coordination site shows slightly lower energy (0.029 eV) than that of the fourfold coordination site. This difference could be due to the smaller size of Li than Na. In both cases the basic structure of Si$_{10}$, which is tetracap trigonal prism, remained almost unaffected. The smallest distances between the M and Si atoms for LiSi$_{10}$ and NaSi$_{10}$ were found to be 2.48 and 3.01 Å, respectively. The calculated interaction energies of Li and Na atoms with Si$_{10}$ are 1.70 and 1.24 eV, respectively.

The electronic configuration of Be and Mg atoms is $1s^2 2s^2$ and $1s^2 2s^2 2p^6 3s^2$. It is clear from their electronic con-

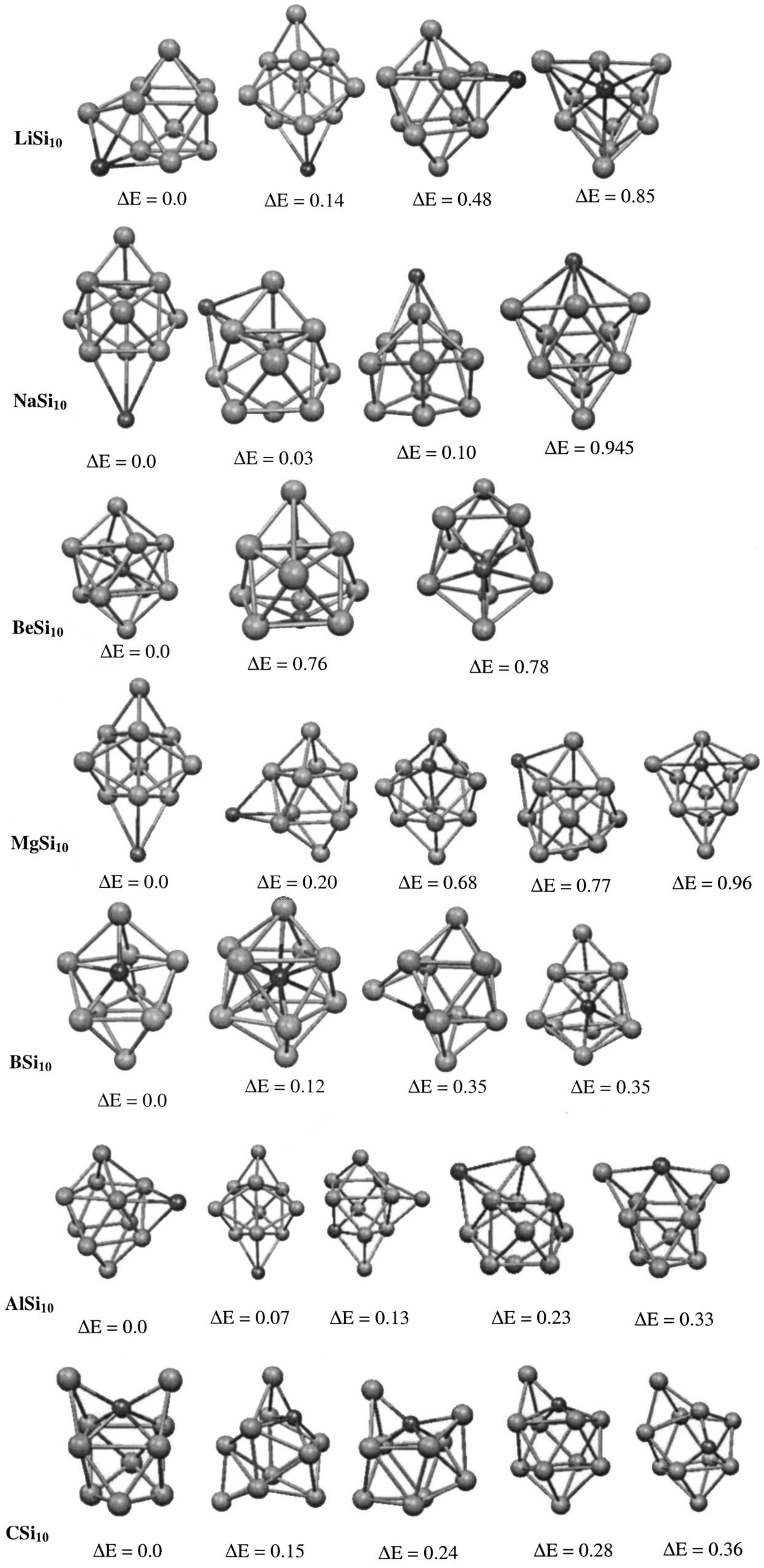

FIG. 2. Low-lying isomeric structures (within 1 eV energy difference) of $M\mathrm{Si}_{10}$ clusters (M=Li Na, Be, Mg, B, Al, and C) obtained by using the *ab inito* molecular dynamics simulation under the GGA exchange-correlation energy functional. The dark color atom represents the impurity atoms and the atoms with lighter shade correspond to the Si atom. The relative stabilities of each isomer have been expressed in terms of the difference in total energy with respect to the lowest energy isomer.

figuration that the outermost valence orbital is filled and a symmetric charge distribution around these atoms is thus expected. In Fig. 2 we have shown a few low-lying isomeric structures of BeSi_{10} and MgSi_{10} clusters. It has been found that for the BeSi_{10} cluster the lowest energy isomer favors bicapped tetragonal antiprism of ten Si atoms encapsulating one Be atom at the center of it. The distance between the Be atom and Si atoms placed at the corners of the tetragonal antiprism is found to be 2.21 Å and the distance between the Be atom with two vertex atoms is 2.57 Å. The interaction energy of the Be atom with that of the Si_{10} cluster is estimated to be 3.38 eV. Other isomers of the BeSi_{10} cluster lie significantly higher in energy. For the Mg doped Si_{10} cluster the lowest energy structure shows penta-capped trigonal prism where the Mg atom is capping one of the triangular faces from outside. This structure is similar to that of the $\mathrm{Si}_{11}-\mathrm{D}$ isomer. The distance between the Mg and Si atoms is 2.83 Å. The interaction energy of the Mg atom with the Si_{10} cluster has been calculated to be 0.9 eV, which is significantly lower than that of Be interaction energy. This is attributed to the higher coordination of the Be atom being at the center of the Si_{10} cage. From the relative energy differences between the low-lying isomers it has been found that, unlike the BeSi_{10} cluster, the potential energy surface of the MgSi_{10} is relatively flat, consisting of many swallow minima.

The electronic configuration of the B and Al atom is $1s^2 2s^2 2p^1$ and $1s^2 2s^2 2p^6 3s^2 3p^1$. Thus in these clusters the interactions would primarily be governed by the *p*-*p* interactions instead of *s*-*p* as discussed in the above two cases. Figure 2 shows a few low-lying isomers for BSi_{10} and AlSi_{10} clusters. The lowest energy isomer of the BSi_{10} cluster is similar to that of a tricapped tetragonal antiprism of Si_{11} where B has replaced one of the Si atoms from its tetragonal face away from the Si atom capping the trigonal face of the $\mathrm{Si}_{10}-\mathrm{C}$ isomer. The interatomic separation between B and the nearest Si atom is 2.08 Å. Similar structure with different location of B (replacing the Si atom from the tetragonal face adjacent to the Si atom capping the trigonal face) shows 0.351 eV higher in energy. The second higher energy isomer of the BSi_{10} cluster, which is 0.124 eV higher in energy, shows that the impurity B atom occupies the central position of the bicapped tetragonal antiprism. Unlike this, the Al atom is not stable inside the cage of the Si cluster. The lowest energy structure of the AlSi_{10} cluster forms tricapped tetragonal antiprism structure where the Al atom is capping one of the triangular faces, similar to that of $\mathrm{Si}_{11}-\mathrm{C}$. Geometry similar to that of Si_{11} lowest energy structure shows 0.33 eV higher in energy for the AlSi_{10} cluster. The interaction energies for the BSi_{10} and AlSi_{10} clusters are calculated to be 5.01 and 1.99 eV, respectively. This indicates that the interaction of B is significantly stronger than that of other impurity atoms. This is due to the combined effect of larger coordination and the strong *p*-*p* interaction energy.

A few low-lying isomers obtained for CSi_{10} clusters are shown in Fig. 2. Although the lowest energy isomer has similar atomic configuration as that for $\mathrm{Si}_{11}-\mathrm{A}$, there are significant differences for the higher energy isomers. The important point we need to mention is that although C is much smaller in size than Si, it does not favor being trapped inside the cage of the Si_{10} cluster as observed for Be and B atoms. The energy of the encapsulated CSi_{10} cluster isomer similar to that of BeSi_{10} is 1.8 eV higher in energy than the corresponding lowest energy isomer. This is attributed to the strong covalent nature of the C−Si bond, which prefers to have less coordination as compared to that of Be and B. The interaction energy of CSi_{10} was calculated to be 5.77 eV, which is found to be the strongest among all other impurity elements discussed in this work.

ENERGETICS

In order to verify the results obtained using the pseudopotential approach taking only the valence electrons into account, we have further reoptimized the lowest energy isomers under the LCAO-MO approach using the hybrid energy functional (B3LYP/6-31G(d)) taking all electrons into account. The results show that at the B3LYP level the geometries are almost similar to those as has been found under the PW/GGA level of calculations. In Table I, we have summarized a comparative illustration of the energetics for all *M*-doped Si_{10} clusters. It is clear from this table that the binding energies obtained using the plane wave pseudopotential approach (PW/GGA) are overestimated as compared to the B3LYP level of theoretical approach showing similar trend in both cases. In order to avoid any confusion in the following section we will discuss the energetics of these clusters obtained from the more accurate B3LYP level of calculations only.

In order to understand the bond strength for each *M*−Si bond we have optimized the interatomic separations of the corresponding dimers. The calculations have been performed for all possible multiplicity values and the results are summarized in Table I. It is seen that higher multiplicities are always favored for all these dimers. The bond strength of C−Si is the highest and it varies in the order of $\mathrm{C-Si}>\mathrm{B}>\mathrm{Si}>\mathrm{Si-Si}>\mathrm{Al-Si}>\mathrm{Li-Si}>\mathrm{Be-Si}>\mathrm{Na-Si}>\mathrm{Mg-Si}$. From these results two things are evident, i.e., (i) *p*-*p* interaction is stronger than *s*-*p* interaction and (ii) lighter elements bind more strongly than heavier ones. Interestingly, a similar trend in the stability order has been observed for $M\mathrm{Si}_{10}$ clusters ($\mathrm{CSi}_{10}>\mathrm{BSi}_{10}>\mathrm{BeSi}_{10}>\mathrm{Si}_{11}>\mathrm{AlSi}_{10}>\mathrm{LiSi}_{10}>\mathrm{NaSi}_{10}>\mathrm{MgSi}_{10}$). This leads one to infer that, apparently, the incorporation of impurity elements in the host Si cluster is very local in nature. The only exception is found for the BeSi_{10} cluster, which is even more stable than the Si_{11} cluster. This extra stability of BeSi_{10} is attributed to the encapsulation of the Be atom inside the cage of the Si_{10} cluster leading to formation of more symmetric structure. Based on the average binding energies calculated for these clusters, it is clear that while the addition of Li, Na, Mg, and Al reduces the stability of the Si_{10} cluster, Be, B, and C atoms enhance the stability of the Si_{10} cluster significantly. The corresponding values of the interaction energies for Be, B, and C is 2.89, 4.29, and 5.09 eV, respectively.

In order to further understand the nature of interactions of the impurity elements with that of the Si_{10} cluster, we have plotted the energy values of the HOMO and LUMO levels for $M\mathrm{Si}_{10}$ clusters and compared them with that of the Si_{10}

TABLE I. The average binding energy (eV) and interaction energy (eV) of the M atoms with Si_{10} cluster, and the smallest interatomic separations of the $M-Si$ bonds are listed for the lowest energy isomers of MSi_{10} clusters and their respective dimers. The notation "PW/GGA" and B3LYP indicate values obtained using the plane wave based pseudo potential method and LCAO-MO approach, respectively. The column "2S+1" represents the spin multiplicities of the respective dimers.

System	BE (PW/ GGA)	BE (B3LYP)	E_{int} (PW/ GGA)	E_{int} (B3LYP)	$M-Si$ (a.u.)		BE (B3LYP)	$M-Si$ (a.u.).	2S+1
$Li-Si_{10}$	**3.60**	**3.03**	**1.70**	**1.46**	2.48	Li−Si	1.21	2.58	2
							1.55	2.39	4
$Na-Si_{10}$	**3.56**	**2.99**	**1.24**	**1.08**	3.03	Na−Si	0.92	2.87	2
							1.18	2.72	4
$Be-Si_{10}$	**3.75**	**3.16**	**3.38**	**2.89**	2.21	Be−Si	0.59	2.12	1
							1.43	2.12	3
$Mg-Si_{10}$	**3.53**	**2.94**	**0.88**	**0.44**	2.83	Mg−Si	−0.07	2.56	1
							0.88	2.58	3
$B-Si_{10}$	**3.90**	**3.29**	**5.015**	**4.29**	2.08	B−Si	2.28	1.83	2
							3.25	1.92	4
$Al-Si_{10}$	**3.63**	**3.05**	**1.99**	**1.67**	2.53	Al−Si	1.52	2.68	2
							2.32	2.45	4
$C-Si_{10}$	**3.97**	**3.36**	**5.77**	**5.095**	2.01	C−Si	2.83	1.84	1
							4.16	1.72	3
$Si-Si_{10}$	**3.73**	**3.13**	**3.10**	**2.56**	2.42	Si−Si	**2.91**	2.175	3
Si_{10}	3.79	3.18			2.37				

host cluster (Fig. 3). It is observed that, in general, the addition of an atom to the Si_{10} cluster shifts the HOMO energy level upwards (less negative). This is due to the higher HOMO energy level of the impurity atoms, which favors small charge transfer from the impurity atom to the Si_{10} cluster. However, an opposite trend is observed for the substitution of Be and C atoms in the Si_{11} host cluster. The resulting difference between the HOMO and LUMO energy level (HLG) is used as a parameter to indicate the stability of a cluster. For Be and C atom substitution, the HOMO energy level of the Si_{11} cluster becomes more bound (more negative) and thereby increases the energy gap between the HOMO and LUMO energy levels leading to the higher stability of these clusters.

CONCLUSION

In this work we have carried out the geometry optimization for M atom (M=Li, Be, B, C, Na, Mg, Al, and Si) doped Si_{10} clusters using density functional theory under the gener-

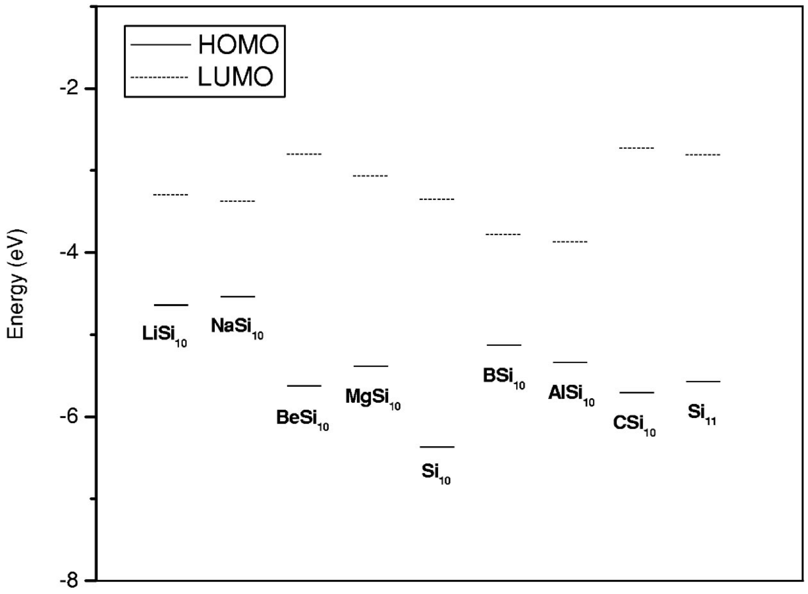

FIG. 3. Comparison of the energy eigenvalues of the HOMO (solid lines) and LUMO (dotted lines) energy levels of MSi_{10} clusters calculated using the LCAO-MO approach at the B3LYP/6-31G(d) level.

alized gradient approximation for the exchange correlation effects. The atomic configurations of the lowest energy isomers obtained at the DFT level were further used to calculate the total energy at the B3LYP/6-31G(d) level of theory. The comparison of the energetics between these two methods suggests that while the GGA formalism overestimates the binding energies, B3LYP results provide underestimated values. The ground state structures of $M\mathrm{Si}_{10}$ clusters indicate that the location of the impurity atom on the host cluster depends on the atomic size and nature of interaction between the host cluster and the impurity atoms. It has been observed that for the BeSi_{10} cluster, the Be atom goes inside the cage of the Si_{10} cluster and forms highly symmetric close packed structure with large gap between the HOMO and LUMO energy levels. Also for the BSi_{10} cluster, the B atom can diffuse into the center of the Si_{10} cage, which is 0.12 eV higher in energy than the lowest energy isomer. In contrast to this, the geometries of other $M\mathrm{Si}_{10}$ clusters become unstable when a M atom is placed inside the Si_{10} cage in spite of having smaller size (C atom) or similar electronic configurations (Mg). The stability of the M-doped Si_{10} clusters has been illustrated from the average binding energies which shows the trend as $\mathrm{CSi}_{10} > \mathrm{BSi}_{10} > \mathrm{BeSi}_{10} > \mathrm{Si}_{11} > \mathrm{AlSi}_{10} > \mathrm{LiSi}_{10} > \mathrm{NaSi}_{10} > \mathrm{MgSi}_{10}$. The interaction energies between the impurity atom and the host cluster also follow a similar trend. Based on these results, it is inferred that while the interactions of Li, Na, Mg, and Al reduce the stability of the Si_{11} cluster, C, B, and Be atoms enhance it more efficiently that Si atom addition.

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