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Isomeric structures and electronic properties of A_4B_4 (A,B=Na, Mg, Al, and Si) binary clusters

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The equilibrium geometries and energetics of the A_4B_4-type binary clusters consisting of Na, Mg, Al, and Si atoms have been calculated using *ab initio* molecular-dynamics simulation under the framework of density-functional theory with the plane-wave-based pseudopotential approach. Several local minima were found to lie close in energy in the potential-energy surface, suggesting a rich variety of isomers for these binary clusters. Further, optimization of the local minimum structures has been carried out by taking all electrons into account using the linear combination of atomic orbitals approach with nonlocal approximations for the exchange-correlation effect. The stability aspects of these clusters have been analyzed based on different parameters such as binding energy, ionization potential, and the energy gap between the highest occupied and lowest unoccupied molecular orbitals (HLG) obtained from the energetics of the neutral and cation clusters corresponding to the lowest-energy structures. The results reveal that for such heteroatomic systems, there is no direct correlation between the binding energies and the ionization potentials or the HLG's for these binary clusters. The charge-transfer analysis has been carried out to understand the bonding nature of these hetreroatomic systems. The results suggest that while bonding between Na, Al, and Si atoms involves significant charge transfer, the Mg atom interacts very weakly. This is further corroborated from the heat of formation of these mixed clusters. While mixing between Na_4, Al_4, and Si_4 tetramer clusters is highly exothermic, mixing of the Mg_4 cluster is less exothermic. The enthalpy of mixing is in the order of $Al_4Si_4 > Na_4Si_4 > Na_4Al_4 > Mg_4Al_4 > Mg_4Si_4 > Na_4Mg_4$.

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INTRODUCTION

The growth of novel materials with tailored physicochemical properties has been one of the most active research areas for the past decade.[1–3] The Agglomeration of a few atoms or molecules forms clusters whose physicochemical properties are found to depend on their size and shapes. Some clusters are found to be more stable than their neighboring clusters and are referred to as magic clusters, which may be used as building blocks to develop novel materials. Small clusters are mostly composed of surface atoms, and a proper knowledge of the electronic structure and geometry of these clusters is important to elucidate their physicochemical properties, such as chemical reactivity, optical absorption spectroscopy, fragmentation behavior, etc. To the best of our knowledge, presently no experimental techniques are available to directly determine the structure of small clusters. Infrared or Raman spectroscopy can be used for very-small-sized clusters, but the analysis of data becomes cumbersome as cluster size increases. Therefore, a detailed theoretical study is important to determine their equilibrium geometry and electronic properties, and a subsequent comparison with experimental results can give an idea about the accuracy of the theoretical models. A larger number of theoretical studies have been performed to investigate the geometries of homoatomic clusters of Na_n, Mg_n, Al_n, and Si_n.[4–28] The results suggest that each type of cluster prefers different structural arrangements in their equilibrium geometries. This has been attributed to the difference in the number of valence electrons present in these clusters, which is reflected in the different nature of bonding.

Although a large number of experimental and theoretical studies are availabale for homoatomic clusters, only a few are reported for mixed metal clusters. The study of mixed metal clusters is of fundamental importance to understand the bonding characteristics and spatial distribution of the constituent atoms. Kanhere and co-workers[29–31] have carried out a number of theoretical studies of impurity-doped metal clusters comprised of monovalent and divalent metal atoms. The results suggest that depending on the atomic radius and the nature of chemical bonding, the impurity atom can be trapped inside the host cluster or segregate outside. Another interesting aspect of a mixed metal cluster is to understand the atomic distribution of different elements when two homoatomic clusters are mixed together.

Cluster aggregates composed of two types of elements with different electronic configurations are referred to as binary clusters. Several studies are available on the II-VI and III-V semiconductor clusters, which have been studied using localized atomic basis sets.[32–35] These clusters are called compound clusters due to the existence of strong bonding between the constituent elements with a large difference in their electronegativity. These can be compared with the intermetallics in the bulk, which are formed for a fixed composition.

Mixing of two or three elements with varying compositions forms bulk alloys. Quite often it has been observed that the two elements, which are not miscible in the bulk, can form small cluster aggregates. This is because the strain produced in the alloy formation due to size mismatch is considerably reduced for the cluster. Such clusters with significantly high binding energies can be visualized as the building blocks for the formation of new materials with properties quite different from that of their corresponding alloys. However, predicting geometries of such mixed clusters is difficult due to the large number of possible isomers

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forming a rather flat potential-energy surface. Ballone *et al.*[36] have studied the ground-state geometries of $Na_{10}K_{10}$ mixed alkali-metal clusters. In this system, both Na and K atoms belong to the same group of the Periodic Table with a single valence electron. The segregation of K to the surface of the $Na_{10}K_{10}$ cluster was understood in terms of the larger size of K as compared to Na. This tendency has also been observed for mixed Li-Na clusters.[37] However, this behavior is in contrast with the observed behavior of bulk liquid phase where both Na and K are completely miscible. Recently Akola *et al.*[38] have studied the geometries and electronic properties of lithium-rich Al_nLi_{5n} $(n=1-6,10)$ clusters using first-principles simulations. It has been observed that for small clusters, Al forms a compact inner core configuration which changes into a chainlike skeleton embedded in a lithium surrounding as the cluster size increases.

Previously, we have investigated the equilibrium geometries of mixed clusters with 4:4 and 6:8 composition using molecular-dynamics simulation under the orbital-free density-functional-theory formalism.[39,40] However, due to the neglect of orbital contributions, this method was not able to predict the Jahn-Teller distortion effects on the geometries of these clusters. Tetracap tetrahedron geometry was obtained as the lowest-energy configurations for all A_4B_4 (A and $B=$Li, Na, Mg, Al, Si, Sb, Sr, etc.) clusters irrespective of the elements involved. Alonso *et al.*[41] have shown that for all A_4Pb_4 ($A=$Li, Na, K, Rb, and Cs) clusters, Pb_4 units form an inner tetrahedron structure whose faces are capped by alkali-metal atoms. Recently, Chacko *et al.*[42] have studied the structural and the electronic properties of several aluminum-based binary clusters (Al_4X_4, $X=$Li, Na, K, Be, and Mg) using the plane-wave pseudopotential method.[43] It is found that the ground-state structures of these clusters are not tetracap-tetrahedrons, rather they differ depending on the electronic configuration of the elements involved.

In this paper, we report the ground-state geometry and electronic structure of A_4B_4 clusters comprised of Na, Mg, Al, and Si atoms, which belong to the same period with an increasing number of valence electrons in the outermost shell. The objective of this study is twofold. First, we would like to find out several possible isomeric structures of these clusters based on their total energies. Secondly, we would like to understand the stability aspects of these binary systems based on different physicochemical properties, such as binding energy, ionization potential, the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gap (HLG), and the enthalpy of mixing between two homoatomic tetramer clusters. In order to generate background information relevant to understand the chemical bonding in binary clusters, we have done these calculations in multiple steps with an increasing number of atoms in the cluster. In the first step, we have calculated homoatomic dimers (A_2) of these elements and compared their bond lengths and binding energies with the experimental values. After this, we have carried out similar calculations for heteroatomic dimers (AB). In the third step, we have calculated the ground-state geometries and energetics of homoatomic tetramer clusters (A_4). Finally, we have calculated the geometries and energetics of bimetallic A_4B_4 clusters consisting of Na, Mg, Al, and Si atoms. The results of the dimers and tetramers are useful to understand the growth mechanism of binary A_4B_4 clusters.

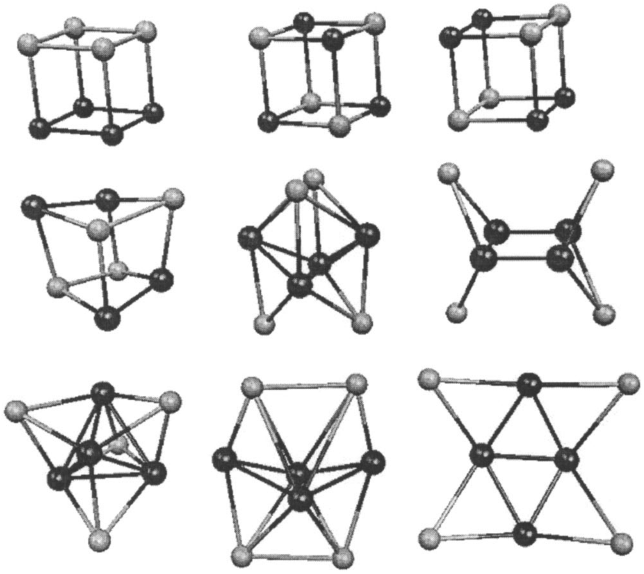


FIG. 1. Starting geometries of A_4B_4 clusters considered to obtain the equilibrium geometries.

COMPUTATIONAL DETAILS

For dimers and tetramers, the geometries and the total energies were optimized under the spin-polarized density-functional theory using the linear combination of atomic orbitals (LCAO) approach.[44] A standard 6-31G (d,p) basis set was employed[45] for this purpose. The exchange correlation energy was calculated using Becke's three-parameter functionals.[46] This functional uses part of the Hartree-Fock exchange and Becke's exchange functionals and the Lee-Yang-Parr[47] correlation functional.

For binary A_4B_4 clusters, we have adopted two-step optimization to obtain the lowest-energy structures. In the first step, density-functional theory combined with molecular-dynamics simulations was used to locate several local minimum structures on the potential-energy surface.[48] The equilibrium geometries of each binary cluster were obtained by heating several initial configurations (shown in Fig. 1) up to 800 K followed by equilibration at this temperature for $\sim$2.5 ps so that a reasonable phase space could be spanned. Finally, the cluster was slowly cooled at 0 K and forces were minimized up to 10^{-4} a.u. to obtain the equilibrium structure. Briefly, this method uses first-principles pseudopotentials for the electron-ion interaction and a plane-wave basis set to represent the wave function. The pseudopotentials used in the present calculations are based on the norm-conserving pseudopotentials of Bachelet *et al.*[49] with the Kleimann and Bylander decomposition.[50] The exchange correlation energy was calculated using the local-density approximation (LDA) with the parametrized form of Ceperley and Alder.[51]

In order to reconfirm the lowest-energy isomers, some of the local minima were further relaxed using the LCAO-MO (molecular orbital) approach as has been applied for dimers

TABLE I. The bond lengths in homoatomic and heteroatomic dimers, contraction in bond lengths, and the binding energies are listed in this table. The experimental values of the bond length and binding energies for homoatomic dimers are shown in parentheses. The atomic radii (R_A and R_B) used in determining the contraction of bond length (ΔR) were taken from Ref. 52.

System	R_e (Å)	R_A+R_B	ΔR	BE/at	Multiplicity ($2S+1$)
Na_2	3.04 (3.07)	3.80	0.76	0.37 (0.36)	1
Mg_2	3.92 (3.89)	3.20	−0.72	0.07 (0.025)	1
Al_2	2.51 (2.46)	2.86	0.35	0.59 (0.67)	3
Si_2	2.17 (2.24)	2.64	0.47	1.47 (1.66)	3
Na-Mg	3.46	3.51	0.05	0.06	2
Na-Al	3.14	3.34	0.20	0.37	1
Al-Mg	2.95	3.03	0.08	0.15	2
Na-Si	2.71	3.23	0.52	0.59	4
Mg-Si	2.57	2.92	0.35	0.44	3
Al-Si	2.44	2.75	0.31	1.16	4

and tetramers. Finally, to calculate the vertical ionization potentials, we have calculated the total energy using the density-functional-theory-based LCAO approach for the neutral and singly positively charged clusters having similar atomic configuration using an identical method and basis set.

RESULTS

The results obtained for homoatomic and heteroatomic dimers are presented in Table I. The calculated bond lengths and binding energies for these clusters show wide variation with the change in the number of valence electrons. These results are useful to illustrate the interaction of two atoms without the influence of many-body effects. In order to assess the reliability of the computational technique used in this study, we have compared our results of the binding energy and bond lengths for homoatomic dimers with the available experimental values[52] as listed in Table I. Good agreement between our results and experimental data increases confidence in the computational method adopted in this study. The large interatomic separation for Mg_2 (*more than the sum of their atomic radii*) indicates very weak interaction between the filled electronic subshells ($3s^2$) of Mg leading to van der Waals bonding (0.07 eV/at). In a recent work, Kaplan *et al.* have discussed it in detail.[53] The weak interaction of Mg atoms is further manifested in the lower binding energies of the heteroatomic dimers involving a Mg atom.

In general, the contraction of bond length is proportional to the overlap of the valence orbitals and thereby the strength of the bonds. In Table I we have listed the contraction of bonds considering the difference between the sum of the atomic radii and the bond lengths. It is seen that for homoatomic dimers the contraction in the bond length is maximum for Na_2 and minimum for Mg_2. However, the bond strength is on the order of $Si_2>Al_2>Na_2>Mg_2$. The larger contraction of Na_2 bond length over Al_2 and Si_2 reflects a larger overlap between the s-s orbitals than the p-p orbitals. For heteroatomic dimers also we see that, except for the Al-Si dimer, the contraction of bond lengths is directly related to their binding energies. For the Al-Si dimer, although the binding energy is very high, the p-p overlap reduces the contraction in their bond lengths.

TETRAMER CLUSTER

The ground-state geometries of homoatomic clusters were optimized starting with different configurations, viz., square, planar rhombus, rectangle, bent rhombus, etc. The results are summarized in Table II. The ground-state geometries of these clusters show that while Na_4, Al_4, and Si_4 prefer rhombus geometry, Mg_4 relaxes into a tetrahedron as the lowest-energy structure. For Na_4 rhombus (smaller bond angle $=51.6°$) structure, the side bond length and smaller diagonal distance were found to be 3.50 and 3.04 Å, respectively, with singlet spin multiplicity ($2S+1$) as the lowest-energy isomer. The triplet state of the Na_4 cluster relaxes to the square planar configuration with a Na-Na distance of 3.35 Å. This is

TABLE II. The smallest interatomic separations, the ground-state geometries, binding energy/atom, ionization potentials, and the HLG values for homoatomic tetramer clusters are represented in this table.

System	Na_4	Mg_4	Al_4	Si_4
R_e (Å)	3.04	3.18	2.58	2.33
Structure	D_{2h}	T_d	D_{2h}	D_{2h}
Multiplicity	1	1	3	1
BE/at (eV)	0.417	0.143	1.24	2.74
IP (eV)	4.32	6.43	6.47	8.13
HLG (eV)	1.27	2.95	1.72	2.42

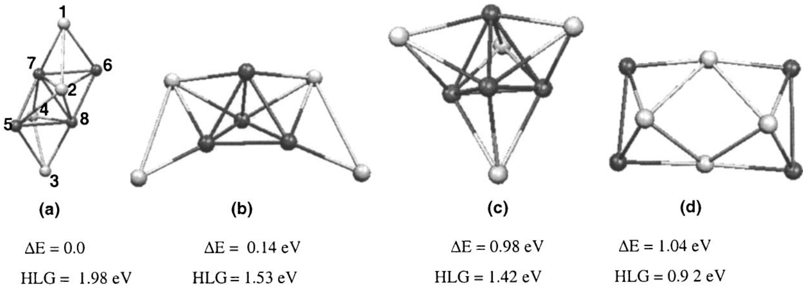


FIG. 2. Isomers of a Na_4Mg_4 cluster with their relative stability in terms of the total energies. The dark circle and light circle correspond to the Mg and Na atoms, respectively.

0.31 eV higher in energy than the rhombus configuration. The lowest-energy structure of the Mg_4 cluster is a regular tetrahedron with 3.18-Å separations between Mg atoms. Interestingly, it is noted that even if we start with a planar configuration, it relaxes back to a three-dimensional tetrahedron structure. This suggests that the Mg_4 cluster favors larger coordination with compact geometry and there is no planar metastable state for this cluster. The significant compression in the bond length of the Mg_4 cluster as compared to the Mg_2 dimer is due to its exceptional high stability. The significant increase in the stability of the Mg_4 cluster could arise due to two reasons: (i) its three-dimensional structure and (ii) the Mg_4 cluster contains eight valence electrons with tetrahedral geometry, which is a magic number as predicted by Alonso *et al.*[41] The magic of the Mg_4 cluster is also evident from its higher IP and HLG values.

For the Al_4 cluster, the planar rhombus (smaller bond angle$=68.9°$) with triplet multiplicity was found to be the most stable configuration. The Al-Al distance for the side arms and short diagonal was found to be 2.58 and 2.92 Å, respectively. The most stable structure for the Si_4 cluster was found to be a singlet with planar rhombus (smaller angle $=62.87°$) geometry. The side bond length is found to be 2.33 Å with the short diagonal length of 2.43 Å. Comparison of these results with previously published results[5,15,54,55] shows good agreement. The trend in the binding energies suggests that as the number of valence electron increases, the bonding becomes strong with the exception of the Mg_4 cluster.

GROUND-STATE GEOMETRY OF THE A_4B_4 CLUSTER

After obtaining fairly good agreement between the present results obtained for dimer and tetramer clusters with those reported earlier, we have carried out detailed calculations for binary clusters of these elements having a composition of 4:4. In general, we have observed that the potential-energy surfaces (PES) of these clusters are rather flat with a variety of local minimum structures with several isomers close in energy. However, in this study we have restricted our discussion only for a few isomeric structures, which are close to the lowest-energy isomer. Another important observation which needs to be mentioned is that all the A_4B_4 clusters presented here show zero magnetic moment $(2S+1=1)$ in their lowest-energy state configuration.

Figure 2 shows the selected low-lying isomers of the Na_4Mg_4 cluster. The lowest-energy isomer for the Na_4Mg_4 cluster [Fig. (2a)] shows two trigonal bipyramids (TBP) fused together sharing a common arm. Each TBP consists of a Na_2Mg_3 unit with two Mg atoms shared by both units. The bond lengths for Mg-Mg, Na-Mg, and Na-Na are 3.12, 3.19, and 3.54 Å, respectively. The binding energy was calculated to be 0.39 eV per atom. Another isomer, where four Mg atoms form a distorted tetrahedron, is found to be 0.14 eV higher in total energy. The distortion in the tetrahedron is due to asymmetric capping of Na atoms on it. A similar structure with Na atoms forming the inner tetrahedron is 0.21 eV higher in energy with respect to the lowest-energy isomer. Two other isomers such as the tetracap tethahedron and the tetracap bent rhombus are found to be very close in energy with a difference of 0.05 eV.

The geometry optimization of the Na_4Al_4 cluster showed a rich variety of isomers with small differences in their total energies, as shown in Fig. 3. The lowest-energy structure shows a bent rhombus (dihedral angle$=157°$) formed by four Al atoms (Al-Al$=2.50$, 2.64, and 2.71 Å for short diagonal, smaller arm, and longer arm, respectively) with one Na atom placed on the top at the bridge position of the short diagonal (Na-Al$=3.12$ Å) and the other three Na atoms capping the edges of the rhombus (Na-Al$=3.05$ Å). The binding energy of this cluster is calculated to be 1.23 eV/at. A planar configuration with higher symmetry where four Al atoms are forming a rhombus and four Na atoms are capping

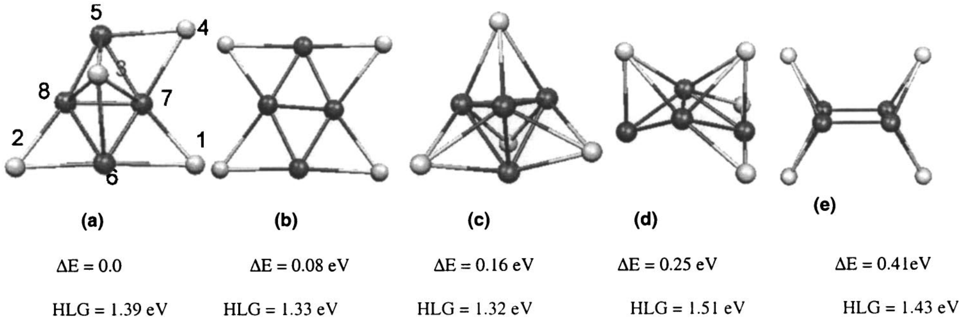
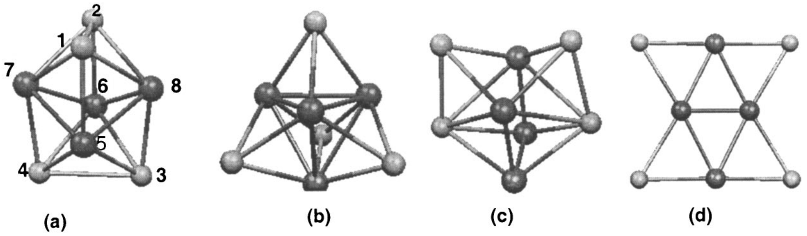


FIG. 3. Isomers of a Na_4Al_4 cluster with their relative stability in terms of the total energies. The dark circle and light circle correspond to the Al and Na atoms, respectively.



ΔE = 0.0 HLG = 2.14 eV

ΔE = 0.57 eV HLG = 2.06 eV

ΔE = 0.60 eV HLG = 1.80 eV

ΔE = 1.66 eV HLG = 1.64 eV

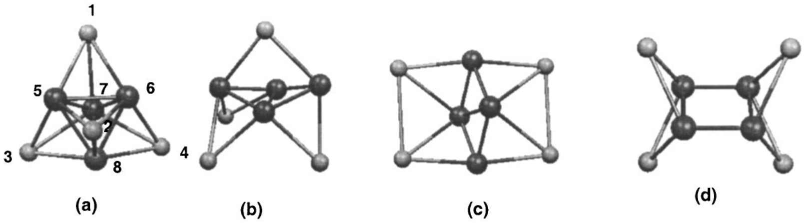
FIG. 4. Isomers of a Mg_4Al_4 cluster with their relative stability in terms of the total energies. The dark circle and light circle correspond to the Al and Mg atoms, respectively.

the edges symmetrically is only 0.08 eV higher in energy. Such small differences in the total energy (0.01 eV higher in binding energy per atom) indicate a probable change in the structure by small external perturbation. The next-higher-energy isomer shows a bent rhombus formed by Al atoms with different types of capping by Na atoms on it. It is important to mention that recently Chacko *et al.*[42] have calculated the ground-state geometry of the Na_4Al_4 cluster using the Born-Oppenheimer molecular-dynamics method under the density-functional theory, where they have found a capped bent rhombus structure of the Al_4 cluster [as shown in Fig. 3(d)] as the lowest-energy minimum. However, we have found that this structure is 0.26 eV higher in energy than the lowest-energy structure obtained by us in this study.

The lowest-energy isomer of the Mg_4Al_4 cluster (Fig. 4) shows a bent rhombus formed by Al atoms and the four Mg atoms are capping it with opposite orientation. The angle of the bent rhombus formed by Al atoms is 115°. The bond lengths between two Al atoms are 2.78 Å (short) and 3.59 Å (longer), respectively. The Mg-Al bond lengths are found to be 2.72 and 2.82 Å. The binding energy of the Mg_4Al_4 cluster has been calculated to be 1.07 eV/at. The smaller binding energy is due to the lower bond strength of the Mg-Al bonds, as is apparent from Table I, where the binding energies of all dimers are listed. It is interesting to note here that although the binding energy of the Mg_4Al_4 cluster is lower than the Na_4Al_4 cluster, it has a significantly higher energy gap between the HOMO and LUMO energy levels. This is attributed to its 20 valence electrons, which corresponds to the magic number in the electron shell-filling model. The next two higher energy (0.57 and 0.60 eV with respect to the lowest-energy isomer) isomers of T_d and D_{2d} symmetry are almost isoenergetic as they differ in total energy by only 0.03 eV.

Among various possible local minimum structures, the lowest-energy isomer of the Na_4Si_4 (Fig. 5) cluster forms a tetracapped tetrahedron with four Si atoms forming the inner core tetrahedron and Na atoms are capping the triangular faces from outside. The Si-Si and Na-Si bond distances are found to be 2.49 Å and 2.85 Å, respectively. The structure is spherically symmetric. The binding energy of this structure is calculated to be 2.02 eV/at. This is significantly higher than the previous three binary clusters. The enhanced stability of this cluster can be explained due to a large charge transfer from the alkali metals to the Si_4 cluster with tetrahedral geometry, which results in a 20-electron magic number cluster. This further corroborates the explanation provided in an earlier work by Alonso *et al.*,[41] where they have illustrated the stability of a tetrahedral geometry of group IV elemental clusters using the electronic-energy-level spectrum. Interestingly, it is noted that although both Mg_4Al_4 and Na_4Si_4 clusters have 20 valence electrons, they differ significantly in their binding-energy values. The significant difference between their binding energies could be understood from their respective electronegativity differences, which is reflected in the bond energies of Mg-Al and Na-Si as represented in Table I. The second-higher-energy isomer, which is a bent rhombus formed by Si atoms and Na atoms capping it from outside, is 1.52 eV higher in energy. From the comparison of total energies of different isomers of the Na_4Si_4 cluster, it is clear that unlike other binary clusters, there are larger differences between the energies of these isomers. This may be attributed to the stronger bond strength of the Na-Si bonds and more charge transfer (details of the charge distribution are discussed later) causing ionic nature of bonding in such clusters.

Four lower-lying isomers of the Mg_4Si_4 cluster are depicted in Fig. 6. The lowest-energy structure of the Mg_4Si_4 cluster consists of a planar rhombus structure formed by Si atoms and Mg atoms capping from two opposite sides. The Si-Si, Si-Mg, and Mg-Mg bond lengths are 2.34, 2.78, and 2.80 Å, respectively. The binding energy of this cluster has



ΔE = 0.0 HLG = 2.39 eV

ΔE = 1.03 eV HLG = 1.52 eV

ΔE = 1.35 eV HLG= 1.17 eV

ΔE = 1.64 eV HLG= 1.39 eV

FIG. 5. Isomers of a Na_4Si_4 cluster with their relative stability in terms of the total energies. The dark circle and light circle correspond to the Si and Na atoms, respectively.

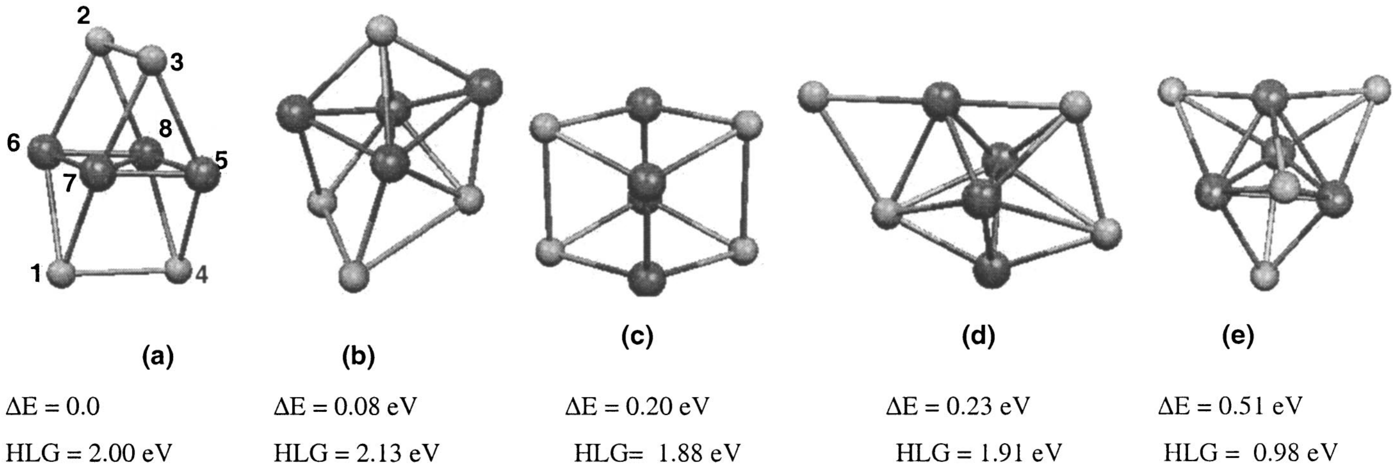


FIG. 6. Isomers of a Mg_4Si_4 cluster with their relative stability in terms of the total energies. The dark circle and light circle correspond to the Si and Mg atoms, respectively.

been calculated to be 1.70 eV/at. Another isomer, which is isoenergetic (~0.08 eV higher in binding energy), consists of Mg atoms capping the bent rhombus formed by Si atoms. This is similar to what has been observed as the second-lower-energy isomer for the Na_4Si_4 cluster. The next-higher-energy isomer is formed by connecting two bent rhombi formed by Mg_2Si_2 units at a distance of 2.45 Å between the two Si atoms. The next-higher-energy isomers show a bent rhombus formed by four Si atoms and Mg atoms cap it differently.

Several starting configurations (shown in Fig. 1), including the one recently reported in Ref. 15, were optimized to get the most stable structure of the Al_4Si_4 cluster. A few low-lying isomers are shown in Fig. 7. The lowest-energy isomer shows a capped planar rhombus structure. Four Si atoms with smaller and longer side arms of 2.41 and 2.61 Å, respectively, form the rhombus, and the Si-Si distance between the short diagonal is found to be 2.51 Å. The smallest distance between Al-Si and Al-Al was found to be 2.46 and 2.58 Å, respectively. Interestingly, the highly symmetric tetracap tetraheron structure with a larger energy gap between HOMO and LUMO energy levels represents the second-lower-energy structure with 0.50 eV higher total energy with respect to the lowest-energy structure. Other isomers are significantly higher in energy and their structures have not been discussed in detail. However, it gives us the information that, like the Na_4Si_4 cluster, the potential-energy surface of the Al_4Si_4 cluster has many deep local minimum isomers with a high activation barrier and therefore the simulated annealing strategy may not always lead to a correct ground-state structure.

The most interesting feature for this cluster is the energy gap that is larger than the corresponding values obtained for the Al_4 and Si_4 tetramers. So far we have discussed 27 isomers of A_4B_4 clusters. In none of the cases have we found the energy gap of a binary cluster being higher than the respective homoatomic tetramers. The detailed discussion of such an enhancement in the energy gap is discussed in the following section.

ANALYSIS OF THE ELECTRONIC PROPERTIES

In order to understand the stability of these clusters, we have analyzed their binding energies, ionization potentials, and the HOMO-LUMO energy gaps as shown in Fig. 8. In general, the ionization potential of a small cluster represents its stability. In this work, we have calculated the vertical ionization potentials of all binary clusters and the results are plotted in Fig. 8(b). Theoretically it is calculated from the difference in the total energies between the neutral and posi-

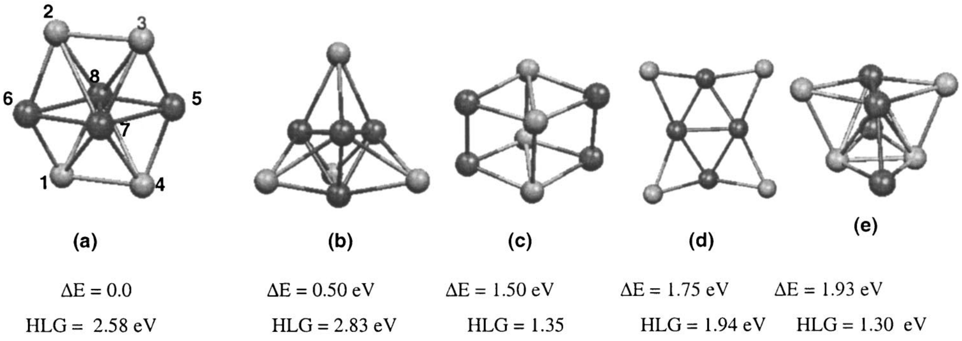


FIG. 7. Isomers of a Al_4Si_4 cluster with their relative stability in terms of the total energies. The dark circle and light circle correspond to the Si and Al atoms, respectively.

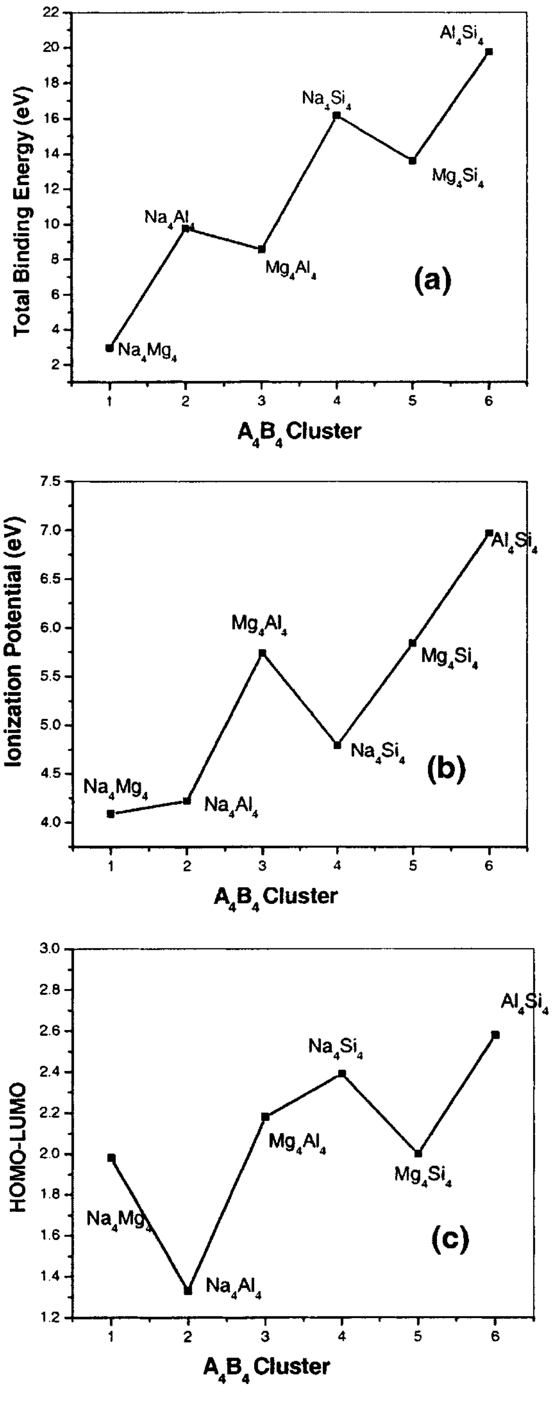


FIG. 8. A comparison of the (a) binding energies, (b) ionization potentials, and (c) energy gaps between the HOMO and LUMO energy levels.

tively charged cluster having the same geometry. For simple metal clusters it has been observed that clusters which exhibit higher stability also show higher ionization potentials, which has been explained in terms of the electron shell model. However, this is not true for heteroatomic systems. For example, although both Mg_4Al_4 and Na_4Si_4 have 20 valence electrons, the comparison of their binding energy and ionization potential shows an opposite trend in their stability. In fact, for all binary A_4B_4 clusters having a Na_4 tetramer (Na_4Mg_4, Na_4Al_4, and Na_4Si_4) there is a significant reduction in their ionization potential values. This fact leads us to infer that alkalization of a cluster reduces its ionization potentials. This is in good agreement with the recent report of Rao *et al.*[16] in which they have shown that the addition of a Na atom significantly reduces the IP's of Al clusters. Therefore, it may be inferred that for binary clusters, higher IP does not necessarily mean higher stability in terms of the binding energy.

The energy gap between the HOMO and LUMO energy levels is considered to be another important parameter, which dictates the stability of small clusters. The larger the gap, the higher is the strength required to perturb the electronic structure. However, distortion of geometry could introduce splitting of the degenerate levels and thereby decrease the energy gap. Figure 8(c) represents the energy gap of the lowest-energy isomers for these mixed clusters. An analysis of Fig. 8 clearly suggests that there is no direct correlation between the binding energies, ionization potentials, and the corresponding energy gaps for such binary clusters. Larger energy gaps are found for Na_4Si_4 and Al_4Si_4 clusters. In general, we have observed that the IP's and HLG values of all these binary clusters are in between their corresponding homoatomic tetramers. Interestingly, we observe an exception to this behavior with Al_4Si_4 isomers. The addition of Al_4 to the Si_4 cluster has increased the energy gap between HOMO and LUMO energy levels. For the Si_4 cluster, the rhombus and tetrahedron structure shows an energy gap of 2.42 and 1.65 eV, respectively, and for the Al_4 cluster the gap is 1.72 eV. The corresponding value of the energy gap for the Al_4Si_4 cluster was found to be 2.58 eV for the lowest-energy isomer. In particular, we notice that the HLG of the TCT structure (2.84 eV) is significantly higher than the Si_4 rhombus (2.42 eV) or tetrahedron (1.66 eV) structure. This is in contrast to our common understanding. We know that in the bulk, Al is a metal and Si is a semiconductor with a band gap of 1.1 eV. Therefore, one would expect the HLG to be reduced when Al_4 is added to the Si cluster. In order to understand the reason for such behavior, we have analyzed the eigenstates of the Si_4 cluster with rhombus and tetrahedral geometry as shown in Fig. 9. It is clear from this energy eigenvalue spectrum that for the high-symmetry tetrahedron structure of the Si_4 cluster, the LUMO is doubly degenerate and the LUMO+1 is triply degenerate and there is a large gap (4.05 eV) between LUMO and LUMO+1 energy levels. The significant increase in the energy gap between HOMO and LUMO energy levels for Al_4Si_4 in the TCT structure implies that the interaction of four Al atoms results in filling of the doubly degenerate LUMO and thereby opens up a large gap. A similar feature was observed when alkali-metal atoms are attached to the tetrahedral unit of the Pb_4 cluster.[41] This behavior provides further evidence of the monovalent behavior of Al atoms for very small clusters due to the large separation between the energy levels of $3s$ and $3p$ orbitals.[17] More interestingly, we have also noticed an increase in the energy gap of the Si_4 cluster even though it retains its rhombus configuration after mixing with four Al atoms. Comparison of the energy eigenvalues between the Si_4 (rhombus) and

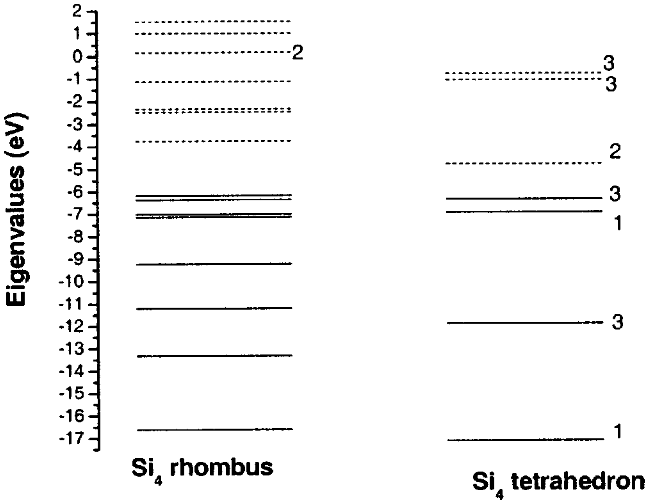


FIG. 9. The eigenvalue spectrum of the Si_4 cluster having rhombus and tetraheron geometry. Solid and dashed lines represent occupied and unoccupied eigenstates, respectively. The number of states which are the same energy (degenerate) are indicated by the integer number placed on the right side of that line.

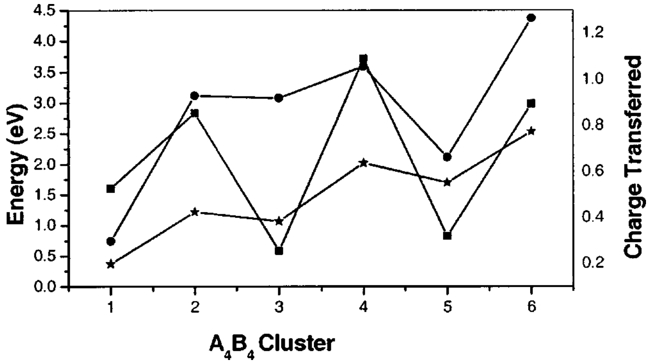


FIG. 10. Binding energies per atom (star), enthalpy of mixing (circle), and the total charge transferred (square) from *A* to *B* atoms are plotted for six mixed valence binary clusters calculated in this work.

the Al_4Si_4 (tetracap rhombus) clusters shows that while the interaction of the Al_4 cluster increases the HOMO energy level of the Si_4 cluster from -6.17 eV to -5.49 eV for Al_4Si_4 (an increase of 0.68), for the LUMO it increases from -3.75 eV to -2.91 eV (an increase 0.84), thus resulting in a net increase in the energy gap of 0.16 eV in the Al_4Si_4 cluster.

Table III summarizes the results of charge distribution in these clusters obtained from Mulliken population analysis. From this table it is clear that the charge transfer is more for Na_4Si_4, Al_4Si_4, and Na_4Al_4 clusters. Enthalpy of a reaction between two reactants is a parameter which indicates the formation probability of the product. The enthalpy of mixing between tetramer clusters is calculated from the difference between the energy of the mixed binary cluster and the total energies of the individual tetramer clusters. A negative value of enthalpy therefore suggests the miscibility of two tetramers spontaneously. In order to understand the stability of these bimetallic clusters, we have plotted the enthalpy of mixing, binding energies, and the total amount of charge transfer between the two elements for all these binary clusters, as shown in Fig. 10. A qualitative correlation between the binding energies, charge transfer, and enthalpy of mixing is obtained. This suggests that for binary clusters, the stability in terms of binding energy reflects the strength of heteroatomic bonding in binary clusters instead of the number of electrons as described in the electron shell-model theory.

CONCLUSION

Several isomers of binary clusters consisting of Na, Mg, Al, and Si atoms having 4:4 composition have been calculated using the density-functional theory formalism. The stability aspect of such clusters has been discussed in terms of their binding energies, ionization potentials, energy gaps between the HOMO and LUMO energy levels, and the charge-transfer analysis. Based on the results discussed above, the following conclusions have been inferred.

(i) From the geometries and energetics, it has been inferred that these binary clusters have a rich variety of local minima in the potential-energy surface. Regarding the stability of such clusters, a direct correlation between the binding energies, ionization potentials, and energy gaps have not been observed, as is apparent from the results obtained for two binary clusters (Mg_4Al_4 and Na_4Si_4) containing 20 valence electrons. These results suggest that for such binary clusters, the definition of the stability should be clearly ex-

TABLE III. Mulliken population analysis for charge distribution of the lowest energy isomer of A_4B_4 binary clusters calculated in this work.

Na_4Mg_4		Na_4Al_4		Mg_4Al_4		Na_4Si_4		Mg_4Si_4		Al_4Si_4	
Na1	0.0177	Na1	0.2140	Mg1	−0.0644	Na1	0.2742	Mg1	0.0878	Al1	0.1141
Na2	0.2505	Na2	0.2141	Mg2	−0.0641	Na2	0.2742	Mg2	0.0873	Al2	0.1141
Na3	0.0079	Na3	0.2141	Mg3	−0.0642	Na3	0.2742	Mg3	0.0873	Al3	0.1141
Na4	0.2523	Na4	0.2141	Mg4	−0.0639	Na4	0.2743	Mg4	0.0875	Al4	0.1141
Mg5	−0.1132	Al5	−0.1466	Al5	0.0640	Si5	−0.2742	Si5	−0.01537	Si5	−0.0618
Mg6	−0.0639	Al6	−0.1463	Al6	0.0641	Si6	−0.2741	Si6	−0.01551	Si6	−0.0618
Mg7	−0.2017	Al7	−0.2817	Al7	0.0641	Si7	−0.2742	Si7	−0.15960	Si7	−0.2904
Mg8	−0.1495	Al8	−0.2817	Al8	0.0641	Si8	−0.2742	Si8	−0.15958	Si8	−0.2904

pressed in terms of the relevant properties.

(ii) The alkalization of higher valence clusters leads to a decrease in the ionization potential.

(iii) The enhancement of the energy gap of Al_4Si_4 binary clusters as compared to the respective energy gaps of the constituent homoatomic Al_4 and Si_4 tetramers is an interesting observation. This reflects the magic behavior of this cluster with tetrahedral symmetry.

(iv) The enthalpy of mixing for all these clusters is negative and follows the order of $Al_4Si_4 > Na_4Si_4 > Na_4Al_4 > Mg_4Al_4 > Mg_4Si_4 > Na_4Mg_4$.

(v) Finally, the Al_4Si_4 cluster, which has higher values of binding energy, ionization potential, energy gap, and energy of mixing, appears to be the most stable cluster in this series, and it can be used further as a building block to synthesize cluster-assembled materials.

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