Structures and Energetics of Be_nSi_n and $Be_{2n}Si_n$ ($n = 1-4$) Clusters

R. C. Binning, Jr.* and Daniel E. Bacelo*

*Department of Sciences and Technology, Universidad Metropolitana, P. O. Box 21150,
San Juan, Puerto Rico 00928-1150*

Received: September 8, 2004; In Final Form: November 10, 2004

The structures and energies of Be_nSi_n and $Be_{2n}Si_n$ ($n = 1-4$) clusters have been examined in ab initio theoretical electronic structure calculations. Cluster geometries have been established in B3LYP/6-31G(2df) calculations and accurate relative energies determined by the G3XMP2 method. The two atoms readily bond to each other and to other atoms of their own kind. The result is a great variety of low-energy clusters in a variety of structural types.

Introduction

The study of clusters of atoms and molecules has expanded rapidly in the past decade. Interest has waxed as it has become clear that clusters possess chemical[1] and physical[2,3] properties much different from those of the corresponding bulk materials. The small clusters of silicon, which is abundant and the most commercially important semiconductor, have been extensively examined. Beryllium is less studied and less abundant and finds fewer uses, at least partly due to the toxicity of its compounds,[4] but it is used to obtain alloys that are light and rigid.[5,6] The combination of beryllium and silicon is relatively rare in chemistry. The two coexist in several aluminum silicate minerals, the best known of which is beryl, but there seems to be only one example of a molecule having been synthesized with the goal of incorporating a Be−Si bond.[7] Beryllium silicide clusters have hardly been studied at all; indeed, in general binary clusters are less well characterized than pure element clusters, but they might prove to have interesting structural and physical properties, and these should be explored. We have therefore undertaken a theoretical examination of the structures and relative energies of small clusters of beryllium and silicon.

Raghavachari has reviewed much of the theoretical work on small silicon clusters.[8] The minimum energy structures of the clusters of as many as a dozen atoms are well-established.[9,10] For the smallest clusters, five and fewer atoms, Curtiss et al.[11] have established accurate energy ordering. Attention has more recently shifted to clusters of 20−50 atoms, within which it appears that a transition in the geometries of the global minima from prolate to spherical shapes occurs.[12−16] These require systematic searching of the potential surfaces, and simulated annealing[17] and genetic algorithms[18] have both been employed to that end. In some studies beryllium has been added to passivate the clusters.[16]

Beryllium has been more sparsely studied than silicon, although theoretical studies of Be_2 are plentiful. The atom is pseudo-closed-shell, so the diatomic potential well is quite shallow and sensitive to both static (near degeneracy) and dynamic (pair) correlation effects. Røeggen and Almlöf have reviewed the calculations on the diatomic.[19] Sudhakar and Lammertsma[20] explored the geometries of several small clusters in calculations at the second-order Møller−Plesset perturbation theory (MP2) level, and recently Beyer et al.[21] have examined the Be_2-Be_8 cluster geometries in high-quality density functional theory (DFT) calculations. Other groups have examined the structures, electron affinities, and electron detachment energies of specific clusters, and noteworthy among these have been the studies of Be_5 [22] and Be_{13}.[23]

Only two recent studies of beryllium silicides have appeared. Boldyrev and Simons[24] thoroughly examined BeSi in its ground $^3\Sigma^-$ and low-lying excited states in calculations ranging from the Hartree−Fock (HF) level to quadratic configuration interaction with single and double excitations plus perturbative triples (QCISD(T)) using large basis sets. Corkill and Cohen[25] have done local density approximation calculations on the band structures of bulk groups IIA−IV compounds in their natural combining ratio, including Be_2Si. Whereas the other members of the set were found to be narrow-gap semiconductors, Be_2Si proved to be a conductor, a possible indication that bonding in the compound may exhibit interesting qualities. Although compounds of the class are known, Be_2Si has not been synthesized, and its properties therefore have not been experimentally determined. We have begun an exploration of clusters of beryllium and silicon with an examination of the Be_nSi_n and $Be_{2n}Si_n$ ($n = 1-4$) clusters. The stable geometries of these clusters in their ground electronic states have been determined in B3LYP/6-31G(2df) density functional calculations, and their relative energies accurately established in calculations with the G3XMP2 method.

Methods

Starting geometries for optimization of the smaller clusters were arrived at by intuition informed by the stable arrangements of silicon or beryllium clusters. Beginning with the three-silicon clusters, extensive potential surface searches were needed. DFT Monte Carlo simulated annealing (DFT-MCSA) was employed for these. In simulated annealing[26] the temperature is gradually lowered to “freeze” the system in a minimum energy configuration. Lowering the temperature slowly enough yields the global minimum; more rapid annealing locates local minima. In DFT-MCSA[27] geometries are Monte Carlo sampled, and the energy at each step is evaluated in a DFT calculation. We employed the $DMol^3$ program[28,29] for energy evaluations, with Perdew and Wang’s PW91[30] exchange and correlation density functionals and double numerical polarized basis sets.

---

* To whom correspondence should be addressed. Fax: (787) 759-7663. E-mails: binningrc@yahoo.com; um_dbacelo@suagm.edu.

10.1021/jp0459413 CCC: $30.25

TABLE 1: Energies of Be_nSi_n and $Be_{2n}Si_n$ Clusters (Column Contents Described in the Text)

cluster	figure	E_{B3LYP}[a]	$E_{\mathrm{zero\ point}}$[a]	E_{G3XMP2}[a]	$E_{\mathrm{atomization}}$[b]	E_{atom}[b]$/(N-1)$	$\Delta E_{\mathrm{relative}}$[b]
Be		−14.668 937		−14.629 956			
Si		−289.371 989		−288.940 124			
BeSi		−304.095 395	0.001 299	−303.620 599	31.7	31.7	
Be_2Si	1a	−318.835 537	0.004 122	−318.314 886	72.1	36.0	
Be_2Si_2	1b	−608.358 515	0.006 609	−607.405 124	166.3	55.4	0.0
	1c	−608.344 879	0.006 168	−607.394 956	159.9	53.3	6.4
	1d	−608.342 844	0.006 711	−607.393 105	158.7	52.9	7.5
Be_4Si_2	2a	−637.854 297	0.012 407	−636.800 920	251.5	50.3	0.0
	2b	−637.846 120	0.012 615	−636.797 484	249.4	49.9	2.2
	2c	−637.840 322	0.011 848	−636.791 622	245.7	49.1	5.8
	2d	−637.822 430	0.011 313	−636.782 236	239.8	48.0	11.7
Be_3Si_3	3a	−912.621 716	0.012 021	−911.208 695	312.8	62.6	0.0
	3b	−912.609 175	0.011 178	−911.190 506	301.4	60.3	11.4
	3c	−912.591 862	0.010 617	−911.160 273	282.4	56.5	30.4
Be_6Si_3	4a	−956.912 055	0.020 908	−955.344 093	466.9	58.4	0.0
	4b	−956.908 851	0.020 831	−955.342 600	465.9	58.2	0.9
	4c	−956.901 122	0.020 897	−955.338 448	463.3	57.9	3.5
	4d	−956.875 780	0.020 460	−955.318 070	450.5	56.3	16.3
Be_4Si_4	5a	−1216.908 660	0.016 811	−1215.026 131	468.0	66.9	0.0
	5b	−1216.905 886	0.016 925	−1215.023 039	466.1	66.6	1.9
	5c	−1216.903 961	0.016 352	−1215.021 366	465.0	66.4	3.0
	5d	−1216.892 697	0.016 828	−1215.012 287	459.3	65.6	8.7
	5e	−1216.893 253	0.016 398	−1215.010 664	458.3	65.5	9.7
	5f	−1216.881 314	0.016 270	−1215.001 113	452.3	64.6	15.7
	5g	−1216.867 595	0.016 197	−1214.989 828	445.2	63.6	22.8
Be_8Si_4	6a	−1275.967 270	0.031 275	−1273.886 910	682.0	62.0	0.0
	6b	−1275.965 228	0.029 490	−1273.879 117	677.1	61.6	4.9
	6c	−1275.956 931	0.029 261	−1273.876 361	675.3	61.4	6.6
	6d	−1275.954 681	0.029 457	−1273.874 463	674.1	61.3	7.8
	6e	−1275.948 503	0.029 630	−1273.868 464	670.3	60.9	11.6
	6f	−1275.944 168	0.029 854	−1273.863 600	667.3	60.7	14.6

[a] Energies in atomic units. [b] Energies in kilocalories per mole.

Final geometries and harmonic frequencies were obtained in B3LYP/6-31G(2df) optimizations. B3LYP contains Becke's[31] three-parameter exchange functional and the correlation functional of Lee, Yang, and Parr.[32] Calculations were done with Gaussian03.[33] At these geometries the sequence of single-point calculations needed to obtain G3XMP2 energies was carried out. The Gaussian-*n* theories provide accurate relative energies by stepwise correcting the major errors in theoretical calculations, truncation of the basis set, and incomplete recovery of correlation energy. The result should compare with one obtained in a QCISD(T) calculation with a very large basis set, but in considerably less time. G3X theory[34] varies from Gaussian-3 theory[35] in that B3LYP/6-31G(2df,p) geometries and frequencies are employed, rather than the MP2(FULL)/6-31(d) geometries and HF frequencies of the parent theory. G3XMP2 further modifies G3X theory by replacing some MP4 correction calculations with MP2. Considerable savings in time results, with small loss of precision. The mean absolute deviation in G3XMP2 calculations on the extensive G3/99 test set of thermochemical values is reported to be only 0.25 kcal/mol greater than that for the G3X method.[34]

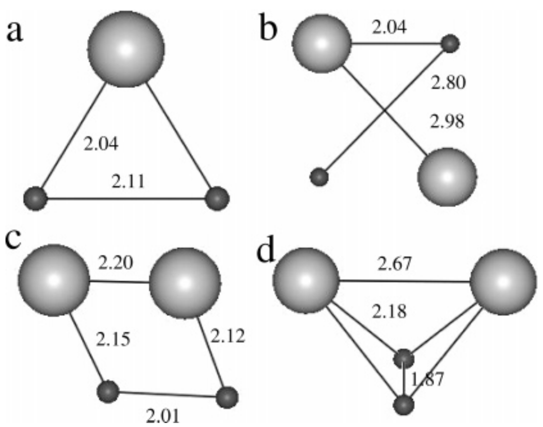

Figure 1. B3LYP/6-31G(2df) optimized structures of Be_2Si and Be_2Si_2. Silicon atoms are larger and lighter in color; beryllium atoms are smaller and darker. Distances are in angstroms.

Results and Discussion

Table 1 lists the calculated ground-state B3LYP/6-31G(2df) and G3XMP2 energies of the clusters, while Figures 1−6 depict the structures of low-energy structures for each cluster. Energy comparisons in the text refer to G3XMP2 energies. In each figure silicon atoms are depicted as larger and lighter in color; beryllium atoms are smaller and darker. The size difference is used to make identification of the atoms easier; the covalent radii of the two are not very different.[36] We shall discuss the clusters ordered by *n*, the number of silicon atoms.

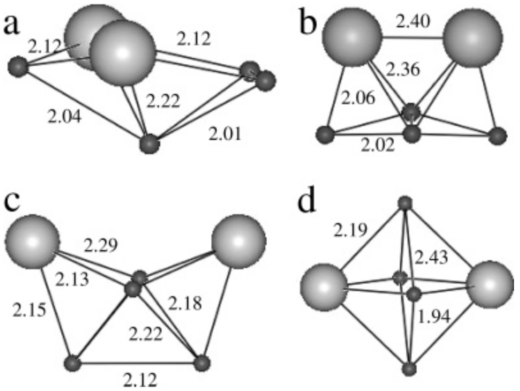

Figure 2. Optimized structures of low-energy Be_4Si_2 clusters.

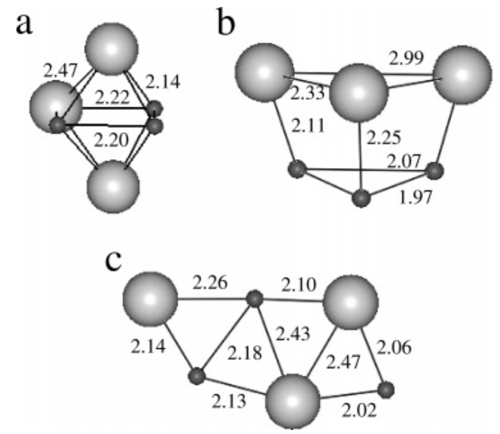

Figure 3. Optimized structures of low-energy Be_3Si_3 clusters.

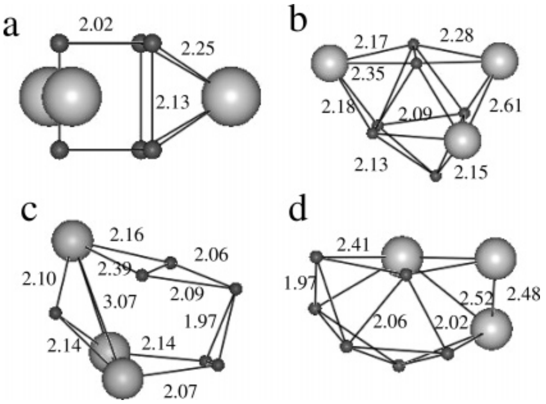

Figure 4. Optimized structures of low-energy Be_6Si_3 clusters.

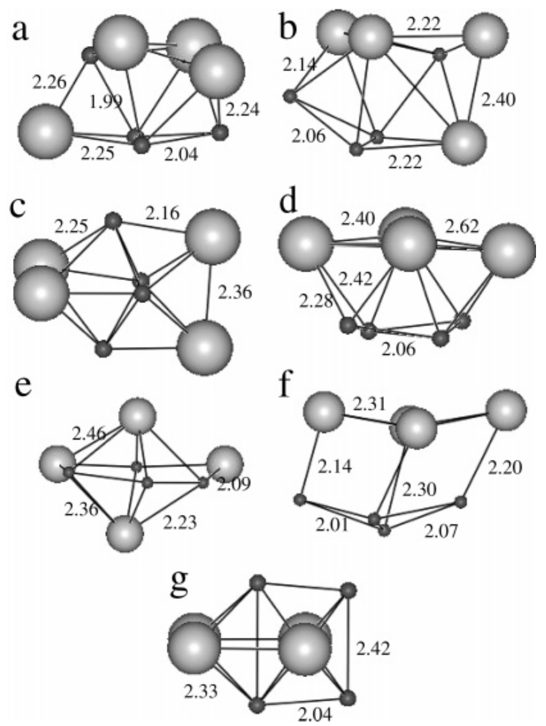

Figure 5. Optimized structures of low-energy Be_4Si_4 clusters.

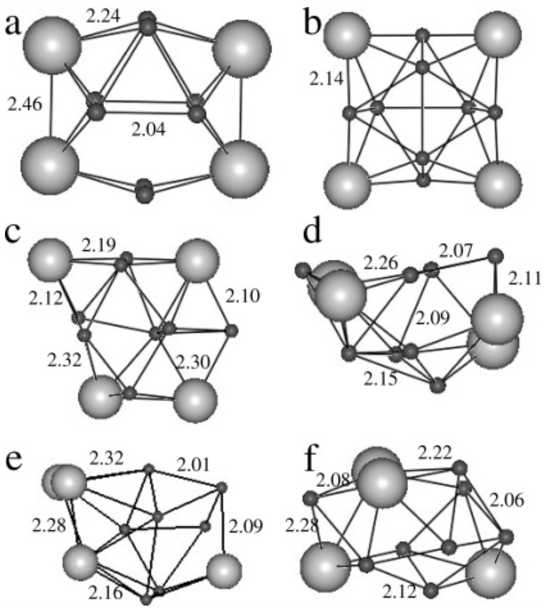

Figure 6. Optimized structures of low-energy Be_8Si_4 clusters.

BeSi and Be_2Si. BeSi has been thoroughly examined by Boldyrev and Simons.[24] They optimized the $^3\Sigma^-$ ground state at the QCISD(T)/6-311+G(2df) level and found the bond length to be 2.14 Å and the bond dissociation energy to be 28.8 kcal/mol. These agree closely with the B3LYP/6-31G(2df) bond length of 2.12 Å and the G3XMP2 bond dissociation energy of 31.7 kcal/mol.

The one stable geometry of Be_2Si is triangular and nearly equilateral. Be_3 [21] is equilateral, while Si_3 [11] has a central angle of 77°. The highest occupied molecular orbital (HOMO) is a π-orbital with significant participation from the out-of-plane p-orbitals of each of the atoms. The Be−Si bonds are polar; population analysis gives a gross charge of −0.30 to Si and +0.15 to each Be. Bond polarity is therefore comparable to that found in HCl, for which the B3LYP/6-31G(2df) gross charges are ±0.27. The dipole moment of Be_2Si is 2.6 D, again indicating significant polarity. At the B3LYP/6-31G(2df) level the ground state of the molecule is $^3B_1$, reversing at the G3XMP2 level to $^1A_1$. The singlet−triplet separation is 24.7 kcal/mol.

Be_2Si_2 and Be_4Si_2. There are three stable Be_2Si_2 structures (Figure 1 b−d). The two lowest lying are planar. The global minimum energy structure is a D_{2h} rhombus of alternating Be and Si, almost square with a Be−Si−Be angle of 94°. Slightly higher in energy (see Table 1) is a second planar quadrilateral (Figure 1c) of paired Be and Si atoms. In this respect Be_2Si_2 follows Si_4, which is also rhombic[11] and has bond lengths of 2.4 Å. Be_4 on the other hand is tetrahedral,[21] with bond lengths of 2.03 Å. Beyer et al.[21] have rationalized the tetrahedral structure of Be_4 as arising from the substantial 2s−2p promotion energy in beryllium, providing an energetic incentive for each atom to form as many bonds as possible. The planar Be_2Si_2 structures are more stable than the nonplanar, despite the fact that in the planar configurations each atom has only two near neighbors. On the other hand in the planar configurations the molecules have a bonding π HOMO that confers stability. The nonplanar isomer (Figure 1d) resembles a distorted tetrahedron or rhombus. It features a pair of widely spaced Si atoms bridged by a pair of Be atoms displaying the shortest bond noted in this study (1.87 Å).

The low-lying Be_4Si_2 isomer (Figure 2 a) is an interesting structure of C_s symmetry consisting of a Be_3Si_2 pentagon capped by a beryllium atom. The pentagon is almost regular; four sides are 2.12 Å in length, the fifth is 2.11 Å, and the Be with two Si neighbors tilts out of the plane by 24.5°. Only 2 kcal/mol in energy above this structure is the one depicted in Figure 2b, a rhombus of berylliums (though slightly bent along the short diagonal) with silicons situated above, forming attached trigonal pyramids and having C_{2v} symmetry. Also low in energy is the structure of Figure 2c, which gives the appearance of the structure of Figure 2b having been folded along the short diagonal of the Be_4 quadrilateral, breaking the Si−Si bond and forming a Be−Be bond. The highest energy structure (Figure 2d) is the most symmetrical (D_{2h}) of the four. It consists of a rectangle of Be atoms with top and bottom caps of Si atoms, resembling a distorted octahedron. The octahedron is the minimum energy structure of both Be_6 and Si_6.[18,21]

Be_3Si_3 and Be_6Si_3. The low-energy Be_3Si_3 cluster (Figure 3a) lies more than 10 kcal/mol below the next most stable cluster found (Figure 3b) and may be seen as two isoceles triangles of the two elements intersecting at right angles or as a distorted octahedron with three atoms of each type at the apexes. Next in stability (Figure 3b) is a structure of Be and Si isoceles triangles, one atop the other and not quite parallel. The last Be_3Si_3 isomer (Figure 3c) is a high-energy planar Be_2Si_3 assembly, with an end cap Be tilted slightly out of the plane.

The global minimum Be_6Si_3 cluster (Figure 4a) is a trigonal prism of berylliums face-capped by silicon atoms. The Be_3 triangles are 2.02 Å on edge, and the prism is 2.13 Å in height. The face-cap silicons themselves form an equilateral triangle 3.96 Å on edge. Each is 2.25 Å from four beryllium atoms. The face-capped trigonal prism is a common structural element in larger silicon clusters.[14] Nearly energetically degenerate with the global minimum is the cluster of Figure 4b that appears to be constructed from two Be_2Si_2 (see Figure 1b) units joined along one edge and connected by Be−Be bonds to a triangle of berylliums. Alternatively it might be viewed as a distorted trigonal antiprism of Be atoms with dual edge caps of Si atoms. Slightly higher in energy is a cluster (Figure 4c) consisting of a Si_3 triangle capped on one side by a Be and on the other by a twisted Be_5 pyramid. The highest energy structure (Figure 4d) contains a pentagon of Be atoms capped on top by another Be and beneath by a nearly equilateral triangle of Si atoms.

Be_4Si_4 and Be_8Si_4. Be_4Si_4 displays a variety of isomeric forms. The three low-energy isomers (Figure 5a−c) are close in energy and structurally related as well. They are perhaps most easily seen as interlaced distorted tetrahedra of silicon and of beryllium. The cluster of Figure 5d lies 8.7 kcal/mol above the global minimum. It consists of a silicon quadrilateral sitting atop a beryllium quadrilateral and is similar to the cluster of Figure 5f. The cluster of Figure 5e consists of an irregular, nearly planar, Be−Si−Be−Si−Be−Be−Be hexagon capped top and bottom by silicons. The double-capped hexagon is a stable silicon cluster.[10] Finally, Figure 5g depicts a high-energy cluster with an interesting structure that appears to be interlaced perpendicular trapezoids of Be and Si.

Be_8Si_4 occurs in an abundance of structures, and the six lowest lying are depicted in Figure 6. Several structural threads run through the examples shown. They are mainly beryllium-centered, with the rhombus or bent rhombus a common element. Most of the external silicon atoms cap beryllium faces and bond to four Be atoms. The global minimum energy structure (Figure 6a) is D_{2h} and appears to be a tetragonal prism of beryllium atoms face-capped by silicon atoms. Actually the Be_4 rhombuses are bent slightly across the short diagonal. The silicons form a rectangle with sides of 2.46 and 3.85 Å. Only 5 kcal/mol above the global minimum is a closely related D_{2d} structure (Figure 6b) in which the Be rhombuses are truly planar. The silicon atoms are arranged in a square, 3.79 Å on edge. The structure shown in Figure 6c is related to the first two, one beryllium being displaced by a silicon at the apex of a rhombus and moving out to bridge two silicons. The structure of Figure 6d retains the feature of the previous structures in that there are four silicon atoms capping a beryllium cluster, but the cluster has mixed features. There is a nearly regular Be_4Si_2 hexagon capped by a Be and joined to a Be_2Si_2 with another Be capping one of the faces. The structure of Figure 6e may again be viewed as a distortion of Figure 6a, but, instead of a tetragonal prism, a beryllium has been removed and one side of the prism has disappeared, the missing beryllium having moved to the opposite side to bridge that. Three silicons act as face caps for this distorted structure, and the fourth is an edge cap. The final structure (Figure 6f) may be seen as being derived from that of Figure 6b with two silicons now acting as end caps rather than face caps and thereby somewhat distorting the Be_8 cluster.

Cluster Energetics. Energy data for the clusters are contained in Table 1. The first column of the table identifies each cluster; the second column, the figure in which its structure is depicted. Columns 3−5 display, respectively, the B3LYP/6-31G(2df,p) energy, the B3LYP/6-31G(2df,p) zero-point harmonic vibrational energy, and the G3XMP2 total energy for each cluster. The three right-most columns of Table 1 show, respectively, the cluster atomization energies, the atomization energies divided by the number of atoms in the cluster less one, and the energy of each cluster relative to the most stable member of its kind. The energies are for singlet states, excepting the Si atom and BeSi, which have triplet ground states.

The B3LYP/6-31G(2df) energy orderings agree closely with the G3XMP2. The exceptions are Be_2Si, where B3LYP predicts a triplet ground state, and in Be_4Si_4, where the order of two clusters (see Figure 5d,e) is reversed. The atomization energies divided by $N_{\mathrm{atoms}} - 1$ provide a measure of the stability of each cluster per added atom. Cluster stability per atom increases with cluster size, but the incremental increases decrease with size. This is expected; the incremental increase should approach zero as clusters approach the bulk solid. Stability per atom appears to alternate between the Be_nSi_n and the $Be_{2n}Si_n$ clusters; $E_{\mathrm{atomization}}/(N_{\mathrm{atoms}} - 1)$ is greater for the 1:1 clusters than for their 2:1 counterparts. BeSi and Be_2Si are exceptional, but here one goes from a one-bond molecule to a three-bond molecule with the addition of an atom. The alternation seems to arise from the fact that each Si contributes twice the number of valence electrons to each cluster as does each Be; thus, the clusters with the lower Be:Si ratio can potentially form more bonds per atom. If we compare Be_6Si_3 with Be_4Si_4, clusters with equal numbers of valence electrons and nearly equal size, we see that the average atomization energies are quite close.

Summary

Both homo- and heteroatomic bonds form easily in the clusters studied, and the result is a variety of low-energy isomers. As a result, although the nominal optimal combining ratio for the two atoms is 2:1, the small $Be_{2n}Si_n$ clusters are not more stable per atom than the Be_nSi_n clusters. Some structural themes are discernible. The low-energy forms of $Be_{2n}Si_n$ are symmetrical arrangements of beryllium atoms face-capped by silicons bonded to four berylliums. In Be_6Si_3 and Be_8Si_4 this type of structure is the global minimum. In Be_4Si_2 the structure that best exemplifies the type (Figure 2d) is not lowest in energy, but in it the two Si atoms must share the same four Be atoms. Bulk Be_2Si should take the antifluorite structure[25] characteristic of groups IIA−IV compounds, with Si atoms in face-centered cubic sites and Be atoms arranged tetrahedrally around them. In going from small clusters to bulk, then, the regions of beryllium clusters capped by silicons will be replaced by clusters with heteroatom nearest neighbors. The nature of the transition toward more bulk-type arrangements promises to be an interesting object for further study. Also of interest is how closely the structures identified here propagate to Be_2X (X = C, Ge, Sn).

Be−Be, Be−Si, and Si−Si bonding are all important in the 1:1 clusters, and the structural theme might be seen as one of interlacing among beryllium and silicon structures. The most stable Be_2Si_2 is a near-square with atoms of alternating type at each corner; the most stable Be_3Si_3 may be viewed as interlaced Be_3 and Si_3 isoceles triangles, and the most stable Be_4Si_4 clusters may be viewed as interlaced distorted tetrahedra. Clusters in which there are separated Si and Be clusters are higher in energy. As with the 2:1 clusters the evolution of structure type with cluster size promises to be an interesting problem for further study.

References and Notes

(1) Valden, M.; Lai, X.; Goodman, D. W. *Science* **1998**, *281*, 1647.

(2) Alivisatos, A. P. *Science* **1996**, *271*, 933.

(3) El-Sayed, M. A. *Acc. Chem. Res.* **2004**, *37*, 326.

(4) Zorn, H. R.; Stiefel, T. W.; Beuers, J.; Schlegelmilch, R. Beryllium Toxicity. In *Handbook on Toxicity of Inorganic Compounds*; Seiler, H. G., Sigel, H., Eds.; Dekker: New York, 1988.

(5) Garvie, L. A. J.; Buseck, P. R.; Rez, P. *J. Solid State Chem.* **1997**, *133*, 347.

(6) The National Aeronautics and Space Administration (NASA) has announced that the next generation James Webb Space Telescope will employ "beryllium-based mirror technology". The press release may be viewed at http://ngst.gsfc.nasa.gov/News/mirror_release.html.

(7) Saulys, D. A.; Powell, D. R. *Organometallics* **2003**, *22*, 407.

(8) Raghavachari, K. *Phase Transitions* **1990**, *24*, 61.

(9) Raghavachari, K.; Rohlfing, C. M. *Chem. Phys. Lett.* **1988**, *143*, 428.

(10) Zhu, X. L.; Zeng, X. C. *J. Chem. Phys.* **2003**, *118*, 3558.

(11) Curtiss, L. A.; Deutsch, P. W.; Raghavachari, K. *J. Chem. Phys.* **1992**, *96*, 6868.

(12) Yoo, S.; Zeng, X. C.; Zhu, X.; Bai, J. *J. Am. Chem. Soc.* **2003**, *125*, 13318.

(13) Zhu, X. L.; Zeng, X. C.; Lei, Y. A.; Pan, B. *J. Chem. Phys.* **2004**, *120*, 8985.

(14) Tekin, A.; Hartke, B. *Phys. Chem. Chem. Phys.* **2004**, *6*, 503.

(15) Ge, Y.; Head, J. D. *J. Phys. Chem. B* **2004**, *108*, 6025.

(16) Grossman, J. C.; Mitáš, L. *Phys. Rev. B* **1995**, *52*, 16735.

(17) Röthlisberger, U.; Andreoni, W.; Parrinello, M. *Phys. Rev. Lett.* **1994**, *72*, 665.

(18) Honea, E. C.; Ogura, A.; Peale, D. R.; Félix, C.; Murray, C. A.; Raghavachari, K.; Sprenger, W. O.; Jarrold, M. F.; Brown, W. L. *J. Chem. Phys.* **1999**, *110*, 12161.

(19) Røeggen, I.; Almlöf, J. *Int. J. Quantum Chem.* **1996**, *60*, 453.

(20) Sudhakar, P. V.; Lammertsma, K. *J. Chem. Phys.* **1993**, *99*, 7929.

(21) Beyer, M. K.; Kaledin, L. A.; Kaledin, A. L.; Heaven, M. C.; Bondybey, V. E. *Chem. Phys.* **2000**, *262*, 15.

(22) Zhao, Y.; Li, S.; Xu, W.-G.; Li, Q.-S. *J. Phys. Chem. A* **2004**, *108*, 4887.

(23) Bauschlicher, C. W.; Petterson, L. G. M. *J. Chem. Phys.* **1986**, *84*, 2226.

(24) Boldyrev, A. I.; Simons, J. *J. Phys. Chem.* **1993**, *97*, 1526.

(25) Corkill, J. L.; Cohen, M. L. *Phys. Rev. B* **1993**, *48*, 17138.

(26) Kirkpatrick, S.; Gellat, C. D.; Vecchi, M. P. *Science* **1983**, *220*, 671.

(27) Bacelo, D. E.; Binning, R. C.; Ishikawa, Y. *J. Phys. Chem. A* **1999**, *103*, 4631.

(28) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508.

(29) Delley, B. *J. Chem. Phys.* **2000**, *113*, 7756.

(30) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(31) Becke, A. D. *J. Chem. Phys.* **1988**, *88*, 1053.

(32) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(33) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

(34) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **2001**, *114*, 108.

(35) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

(36) Alcock, N. W. *Bonding and Structure*; Horwood: Chichester, U.K., 1990.