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Computational Design and Synthesis of Nitrogen-Substituted Carbon and Silicon Clathrates

Kwai S. Chan^{a*}, Michael A. Miller^a, Wuwei Liang^{a,b} and Carol Ellis-Terrell^a

^aSouthwest Research Institute, 6220 Culebra Road, San Antonio, TX 78238, USA; ^bMath Works, 3 Apple Hill Drive, Natick, MA 01760, USA

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A computational approach was utilized to design the framework and to identify potential guest atoms for stabilizing nitrogen-substituted carbon and silicon clathrates. Two new series of N-substituted carbon and silicon clathrates compounds were discovered as potential candidate materials. One of the hybrid C–N clathrates was successfully synthesized using an industrial arc-melting technique. The theoretical bulk moduli of these N-substituted carbon and silicon clathrates were computed and they are comparable to those of C₃N₄, Si₃N₄, and SiC. Some N-substituted carbon clathrates may be suitable for application as hard materials.

Keywords: Hybrid C–N Clathrates, Hybrid Si–N Clathrates, Hybrid Cage Structure, Superhard Materials

Carbon clathrates, which can be considered as analogs of carbon fullerene materials, are composed of C₂₀, C₂₄, and C₂₈ cages linked through SP³-covalent bonds. Theoretical computations have shown that both Type I carbon clathrate (C₄₆) and Type II carbon clathrate (C₁₃₆) may exist as metastable phases under high pressures.[1–3] Like silicon clathrates (Si₄₆),[4,5] Type I carbon clathrates, C₄₆, is predicted to exist in a simple cubic structure that belongs to the space group *Pm* $\bar{3}$ *n*, Number 223, and exhibits a lattice parameter of 6.696 Å.[3] The cage structure of Type I carbon clathrates (C₄₆) is shown in Figure 1. Insertion of guest atoms such as Li, Na, or Ba into the cage structures has been predicted to be feasible under high pressures.[1–3] However, the energies of the formation for the Type I and Type II carbon clathrates are extremely high and neither Type I nor Type II carbon clathrates have been synthesized.

In general, the structure of Type I intermetallic clathrates based on Si, Ge, or Sn can be characterized by a framework of X atoms forming a 3D cage structure.[6–9] Some of the framework atoms can be substituted by elements such as Al, Ga, Cu, and Ag to form a framework that can be represented as M_yX_{46–y}. The empty space within the cage structure can serve as host sites for guest atoms, A. There are two small cages that can host two guest atoms (2a sites) and there are six large cages that can host six atoms (6d sites). Type I clathrates

can generally be described by the formula: A_xM_yX_{46–y}, where A represents the guest atoms and *x* is the number of guest atoms. M represents the substitution atoms on the framework, *y* is the number of the substitution atoms, and X represents the framework atoms. It is also possible for vacancies to exist on the framework. Under this circumstance, Type I clathrates are formally represented as A_xM_yX_{46–y–z}□_z for non-stoichiometric compounds, where □ represents a vacancy and *z* is the number of vacancies on the framework. For simplicity, A_xC_yX_{46–y} is used in this paper to signify both stoichiometric and non-stoichiometric compounds. For non-stoichiometric Type I clathrates, the number of framework atoms is less than 46 and vacancies occur at the site positions of the missing atoms.

The substitution of Type I silicon framework with carbon atoms to form a series of hybrid carbon–silicon clathrates (A_xC_ySi_{46–y}) has been investigated theoretically by Chan et al.[10] The energy of formation of A_xC_ySi_{46–y} has been found to decrease with increasing lattice parameter of the unit cell. Some of these newly discovered Type I hybrid carbon–silicon clathrates (Ba₈C₆Si₄₀, Ba₈C₂₀Si₂₆, and Ba₈C₂₃Si₂₃), which were predicted to exhibit small positive energies of formation, were successfully synthesized utilizing a vacuum arc-melting technique.[10] One implication of the findings of this investigation is that the carbon or silicon

*Corresponding author. Email: kchan@swri.edu, kwai.chan@swri.org

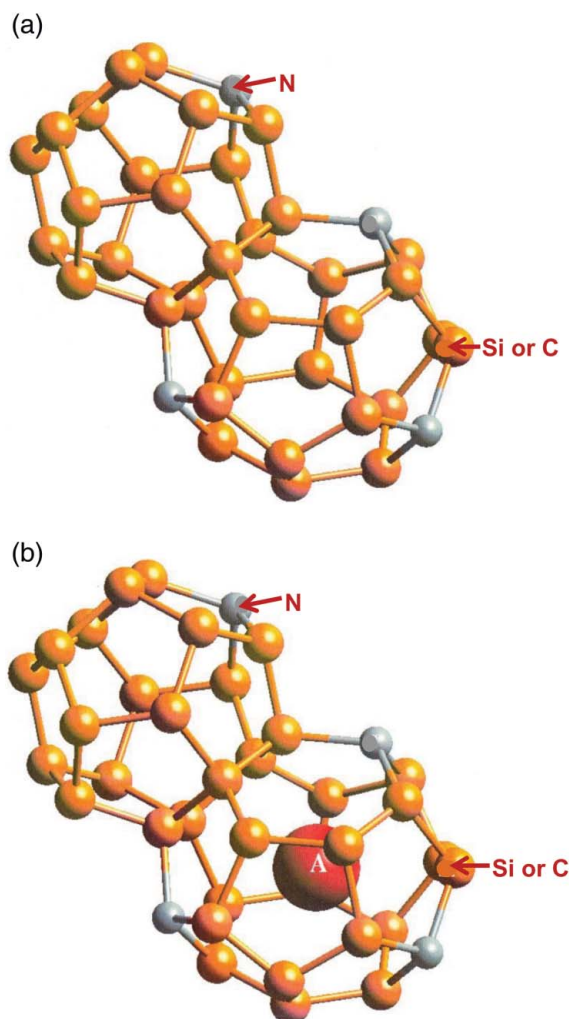


Figure 1. (a) Cage structure of Type I nitrogen-carbon clathrate, N_yC_{46-y} , or nitrogen-silicon clathrate, N_ySi_{46-y} , without guest atoms. (b) Cage structure of Type I guest atom stabilized nitrogen-carbon clathrate ($A_xN_yC_{46-y}$) or nitrogen-silicon clathrate ($A_xN_ySi_{46-y}$) with x number of guest atom A resided within the cage.

framework of Type I clathrates may be reduced and stabilized by substitution of C or Si framework atoms with small-sized atoms.

In this study, Type I hybrid nitrogen-carbon and nitrogen-silicon clathrates were designed by substituting some of the C atoms on the C_{46} framework and some of the Si atoms on the Si_{46} framework with N atoms, respectively. First-principles computational studies using the Car-Parrinello Molecular Dynamics (CPMD) code [11,12] indicate that the carbon atoms in the C_{46} framework can be partially substituted by nitrogen atoms to form a hybrid carbon-nitrogen clathrate, which can be represented by N_yC_{46-y} . Figure 1(a) shows a representation of the Type I N_yC_{46-y} clathrates. Furthermore, guest atoms can be inserted into the cage structure to stabilize the hybrid nitrogen-carbon clathrate by reducing

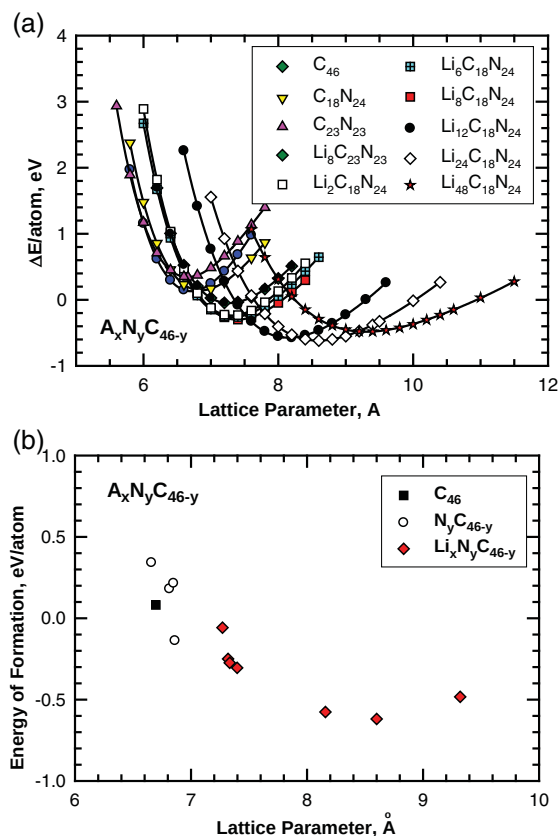


Figure 2. (a) Computed energy curves for Type I $A_xN_yC_{46-y}$ with various amounts of Li guest atoms. (b) A comparison of the energy of formation for C_{46} , N_yC_{46-y} , and $Li_xN_yC_{46-y}$ as a function of lattice parameter.

the energy of formation to form a class of nitrogen-substituted carbon clathrates, represented as $A_xN_yC_{46-y}$. These hybrid structures do not exist in nature and thus represent a novel structure of matter neither known in the open literature nor covered in existing patents on clathrate compounds. Figure 1(b) shows a structural representation of the Type I $A_xN_yC_{46-y}$ clathrate compounds. The influence of Li guest atom ($A = Li$) on the structural stability of the hybrid C-N framework was also considered. Figure 2(a) shows that insertion of Li atoms results in a lowering of the energy formation accompanied by an expansion of the framework for Li atoms ranging from 2 to 48. Table 1 presents a summary of the computed lattice constants and energy of formations for individual Type I clathrate compounds. The computed values of the energy of formation per atom for C_{46} , N_yC_{46-y} , and $Li_xN_yC_{46-y}$ are presented as a function of the lattice parameter in Figure 2(b), which compares the energy of formation for C_{46} and N_yC_{46-y} without and with Li guest atoms. The results in Figure 2(b) show that nitrogen substitution can lower the energy of formation of N_yC_{46-y} compared with that for C_{46} . Furthermore, Li

Table 1. Summary of computed lattice constant, a_0 , and energy of formation, E_f , for Type I clathrate compounds.

Compound	a_0 (Å)	E_f (eV/atom)
C ₄₆	6.6973	.0815
C ₁₈ N ₂₄	6.8622	-.1377
C ₁₉ N ₂₇	6.8148	.1803
C ₂₀ N ₂₆	6.8502	.2144
C ₂₃ N ₂₃	6.6596	.3416
Li ₂ C ₁₈ N ₂₄	7.3192	-.25
Li ₆ C ₁₈ N ₂₄	7.3336	-.2742
Li ₈ C ₁₈ N ₂₃	7.3979	-.3051
Li ₈ C ₂₃ N ₂₃	7.2716	-.0578
Li ₁₂ C ₁₈ N ₂₄	8.1592	-.5765
Li ₂₄ C ₁₈ N ₂₄	8.6003	-.6192
Li ₄₈ C ₁₈ N ₂₈	9.3206	-.4832
Si ₄₆	10.238	.0571
Si ₁₈ N ₂₄	9.0215	-.6338
Si ₂₃ N ₂₃	9.0546	-.5417
Li ₈ Si ₁₈ N ₂₄	9.8924	-.6092

insertion reduces the energy of formation to negative values, which indicates that $\text{Li}_x\text{N}_y\text{C}_{46-y}$ clathrates are stable compounds.

The hybrid nitrogen and silicon clathrate was obtained by substituting some silicon atoms on the Type I silicon clathrate framework, Si_{46} , with nitrogen atoms to produce a nitrogen–silicon framework. As illustrated in Figure 1(a), the hybrid N–Si clathrates framework is represented by $\text{N}_y\text{Si}_{46-y}$ and consists of y nitrogen atoms and $46-y$ silicon atoms with a regular arrangement of 20-atom and 24-atom cages fused together through 5-atom pentagonal rings (Type I clathrate). This compound can be inserted with guest atoms to form $\text{A}_x\text{N}_y\text{Si}_{46-y}$, Figure 1(b). This series of compounds was designed by substituting some of the Si atoms on the Si_{46} framework with N atoms in order to form a Si_3N_4 -like compound with Li guest atoms. The values of the energy of formation for $\text{N}_y\text{Si}_{46-y}$ are compared against those of C_{46} , Si_{46} , and $\text{Li}_x\text{N}_y\text{C}_{46-y}$ in Figure 3. For the compositions considered, the $\text{N}_y\text{Si}_{46-y}$ compounds are stable compounds as their energy of formation values are negative. However, the insertion of Li into the framework causes the lattice to expand, as shown in Figure 3.

Figure 4 is a summary plot that depicts the energy of formation for nitrogen-substituted clathrate compounds, which include $\text{A}_x\text{N}_y\text{C}_{46-y}$ and $\text{A}_x\text{N}_y\text{Si}_{46-y}$, against those of C_{46} , Si_{46} , and $\text{A}_x\text{C}_y\text{Si}_{46-y}$ from Chan et al.[10] Nitrogen substitution is predicted to lower the energy of formation and produces stable carbon and silicon clathrates. These first-principles computations have led to the identification of two new classes of nitrogen-substituted Type I clathrates based on the carbon or silicon framework: (1) N-substituted carbon clathrates without ($\text{N}_y\text{C}_{46-y}$) and with guest atoms ($\text{A}_x\text{N}_y\text{C}_{46-y}$) and (2) N-substituted silicon clathrates without ($\text{N}_y\text{Si}_{46-y}$) and with guest atoms ($\text{A}_x\text{N}_y\text{Si}_{46-y}$).

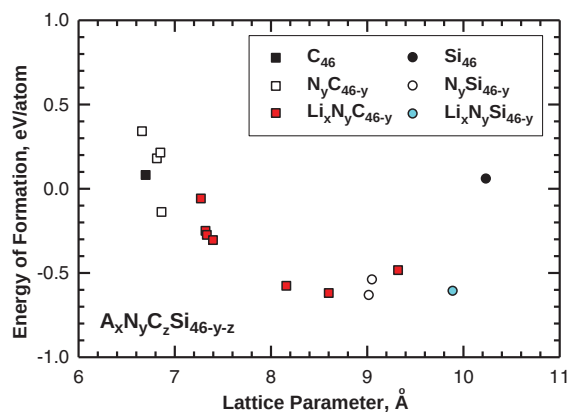


Figure 3. A comparison of the energy of formation for C_{46} , $\text{N}_y\text{C}_{46-y}$, $\text{Li}_x\text{N}_y\text{C}_{46-y}$, Si_{46} , $\text{N}_y\text{Si}_{46-y}$, and $\text{Li}_x\text{N}_y\text{Si}_{46-y}$ as a function of lattice parameter.

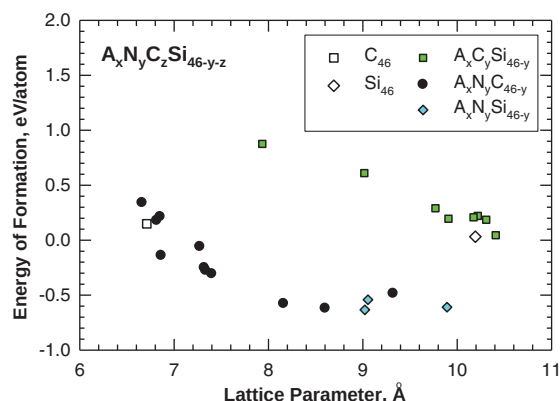


Figure 4. A comparison of the energy of formation for $\text{A}_x\text{C}_y\text{Si}_{46-y}$, $\text{A}_x\text{N}_y\text{C}_{46-y}$, and $\text{A}_x\text{N}_y\text{Si}_{46-y}$ against those of C_{46} and Si_{46} as a function of lattice parameter showing that nitrogen substitution of the framework atoms on C_{46} or Si_{46} results in stable carbon or silicon clathrate compounds. The results for $\text{A}_x\text{C}_y\text{Si}_{46-y}$ are from Chan et al.[10]

The results in Figure 4 also suggest the existence of nitrogen-substituted carbon and silicon clathrates without ($\text{N}_y\text{C}_z\text{Si}_{46-y-z}$) and with guest atoms ($\text{A}_x\text{N}_y\text{Si}_{46-y-z}$) on the basis that nitrogen substitution may lower the energy of formation in both carbon clathrates and silicon clathrates. In a recent study,[10] Ba-stabilized carbon silicon clathrates ($\text{Ba}_8\text{C}_6\text{Si}_{40}$, $\text{Ba}_8\text{C}_{20}\text{Si}_{26}$, and $\text{Ba}_8\text{C}_{23}\text{Si}_{23}$) have been synthesized and shown to exist as metastable phases at ambient temperature. Since Figure 4 shows that the energies of formation for N-substituted carbon and silicon clathrates are lower than those of $\text{A}_x\text{C}_y\text{Si}_{46-y}$, it is likely that nitrogen substitution of the hybrid carbon–silicon framework may lower the energy of formation further to turn them into more stable compounds. It is anticipated that N, C, and Si may form a ternary N–C–Si framework represented by the formula $\text{N}_y\text{C}_z\text{Si}_{46-y-z}$, with $1 \leq y \leq 44$ and $1 \leq z \leq 45 - y$. Furthermore, this new class of new Type I clathrates with mixed nitrogen, silicon, and carbon atoms on the framework of the cage structure may be stabilized by inserting guest atoms

Table 2. Candidate compositions and elemental or alloy starting components for nitrogen-substituted carbon clathrates synthesis by vacuum arc-melting.

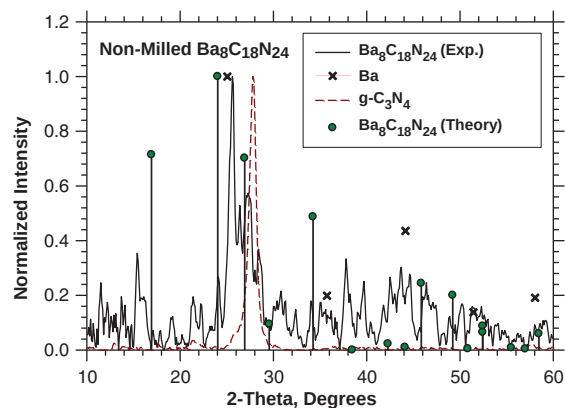
Composition	Target clathrate compound	D (g/cc) FW (g/mol)	Ba	Mg	g-C ₃ N _{4+x} H _y	Total (g/mol) Batch (g)	Estimated density (g/cc)
			3.51	1.74	2.34		Estimated volume (cc)
			137.327	24.305	40.0962		
1	Mg ₈ C ₁₈ N ₂₄	Atom ratio		8	6		
		Weight (g)	0.00	194.44	240.58	435.02	2.07
		Batch	0.00	11.17	13.83	25.00	12.08
2	Ba ₈ C ₁₈ N ₂₄	Atom ratio	8		6		
		Weight (g)	1,098.62	0.0	240.58	1,339.19	3.30
		Batch	20/60	0.0	4.51	25.11	7.61
Total element/batch			20.60	11.17	18.34		

Table 3. Summary of targeted compounds and actual compounds produced by arc-melting.

Composition	Target compound	Actual compounds produced	Type I clathrate
1	Mg ₈ N ₁₈ C ₂₈	MgO, g-C ₂ N ₄ , and MgCN ₂	No
2	Ba ₈ N ₁₈ C ₂₄	Ba, g-C ₃ N ₄ , and Ba ₈ C ₁₈ N ₂₄	Yes (Ba ₈ C ₁₈ N ₂₄)

A inside the cage structure wherein the composition of this series of Type I clathrates is qualitatively represented by the formula $A_xN_yC_zSi_{46-y-z}$, with $1 \leq y \leq 44$ and $1 \leq z \leq 45 - y$, and A can be guest atoms such as Ba, Li, and other similar alkaline and rare-earth metals. Some of the potential compounds in this series of ternary nitrogen, carbon, and silicon clathrates may include Ba_xN₈C₁₀Si₂₃, Ba_xN₈C₁₀Si₂₈, Ba_xN₈C₁₀Si₂₄, Ba_xN₈C₁₄Si₂₄, Li_xN₈C₁₀Si₂₃, Li_xN₈C₁₀Si₂₈, Li_xN₈C₁₀Si₂₄, Li_xN₈C₁₄Si₂₄, and other similar permutations of N, C, and Si. It is noted that vacancies are assumed to be present on the framework of non-stoichiometric compounds when the number of total framework atoms is less than 46. Although not investigated in this study, the presence of vacancies on the framework can significantly affect the electronic properties of these hybrid clathrate compounds.

To validate the first-principles computations, syntheses of Mg₈C₁₈N₂₄ and Ba₈C₁₈N₂₄ were attempted by vacuum arc-melting of admixture of graphitic carbon nitride (g-C₃N_{4+x}H_y) and appropriate metal powders, with detailed compositions shown in Table 2. Synthesis of Li₈C₁₈N₂₄ was not attempted because of difficulties of handling Li metal during arc-melting and the lack of lithium compounds that can be combined to give the desired compositions of Li₈C₁₈N₂₄. In addition, previous first-principles calculations on Li₈C₆Si₄₀ and Ba₈C₆Si₄₀ have also shown that Ba atoms are more effective than the Li atoms in stabilizing the hybrid silicon-carbon framework.[10] Based on prior experience in synthesizing hybrid silicon-carbon clathrates,[10] it was anticipated that Ba would be more effective in stabilizing the hybrid carbon-nitrogen framework and offer a greater chance for a successful synthesis of nitrogen-substituted carbon clathrates. The rationale was borne out

Figure 5. PXRD patterns measured for Composition (2) subsequent to arc-melting of powdered admixture of Ba and g-C₃N_{4+x}H_y.

by attempting to synthesize Mg₈C₁₈N₂₄, which was not successful. Powder x-ray diffraction (PXRD) of the non-milled Mg₈C₁₈N₂₄ powders indicate the absence of any peaks that can be attributed to a Type I clathrate structure and all of the peaks in the PXRD pattern can be identified and attributed to those of the graphitic carbon nitride, MgO, and MgCN₂, as summarized in Table 3.

In contrast, synthesis of Ba₈C₁₈N₂₄ by the vacuum arc-melting technique was successful. In particular, Ba₈C₁₈N₂₄ was synthesized by arc-melting appropriate amounts of Ba and graphitic carbon nitride (g-C₃N_{4+x}H_y) as the starting materials. Admixtures of Ba and g-C₃N_{4+x}H_y (in the proportion of 20.6 g Ba and 4.51 g of g-C₃N_{4+x}H_y powders) were arc-melted to make about 25.11 g of the product, consisting of Ba₈C₁₈N₂₄ plus some amounts of unreacted starting materials. PXRD data of the arc-melted product (i.e. not purified) is presented in Figure 5. Some of the reflection peaks in

the x-ray diffraction (XRD) spectra correspond to unreacted Ba and $\text{g-C}_3\text{N}_{4+x}\text{H}_y$ starting materials. However, the remaining reflections in the XRD spectra do not belong to Ba and $\text{g-C}_3\text{N}_{4+x}\text{H}_y$, and some have been attributed to the Type I clathrate structure in question. The theoretically computed reflections for $\text{Ba}_8\text{C}_{18}\text{N}_{24}$ were obtained by first optimizing the Type I clathrate structures using first-principles CPMD computations to obtain the equilibrium crystallographic parameters, followed by computing the corresponding reflections in the XRD spectrum using the Diamond analysis and visualization software.[13] The comparison indicates that small quantities of Type I clathrate compound are present in the arc-melted $\text{Ba}_8\text{C}_{18}\text{N}_{24}$ product. The crystal structure of this clathrate compound is close to those of $\text{Ba}_8\text{N}_{18}\text{N}_{24}$ based on the characteristic reflections at 2θ of 16.9° , 24.0° , 26.9° , 34.3° , 44.9° , and 49.2° for the nitrogen-substituted carbon clathrate. The products identified by XRD are summarized in Table 3.

The bulk modulus of the various intermetallic clathrate compounds was computed using the first-principles approach according to the expression given by [14]

$$\frac{\Delta E}{V} = \frac{9}{2}B\delta^2, \quad (1)$$

where $\Delta E/V$ is the energy change per unit cell volume, B is the bulk modulus, and δ is the normal strain in the three principal directions of the unit cell. A plot of $\Delta E/V$ versus δ was obtained for each unit cell of individual clathrate compounds and the data were fitted to Equation (1). The regression coefficient was then used to obtain the bulk modulus, B . A summary of the theoretical bulk modulus for various intermetallic clathrate compounds is represented in Table 4.

Also shown in Table 4 for comparison are theoretical or experimental data (indicated by an asterisk) of bulk modulus for diamond, carbon nitride, silicon nitride, and silicon carbide from the literature.[1–3,15–21] The results in Table 4 indicate that a wide range of bulk modulus can be obtained from Type I hybrid C–N, N–Si, and C–Si clathrates, depending on the framework atoms. Some of the carbon clathrate compounds exhibit bulk moduli that are in the range of 245–374 GPa, which are not as high as diamond C or $\beta\text{-C}_3\text{N}_4$, but are comparable to silicon nitride ($\text{C-Si}_3\text{N}_4$) and carbon nitride. Thus, carbon clathrates may be considered for potential applications as hard materials.

First-Principles Computational Method An *ab initio* molecular dynamics code based on the CPMD method [11,12] was utilized to investigate theoretically and systematically the effects of small-atom substitution on the framework and insertion into the empty space inside the cage structure on the energy formation and lattice

Table 4. Computed values of the bulk modulus of selected Type I clathrates compared with theoretical and experimental values of the bulk modulus of diamond, carbon nitride, silicon nitride, and silicon carbide from the literature.

Compound	Structure	B (GPa)
C_{46}	Type I clathrate (Simple cubic)	373.7
		409 [1]
		363.7 [2]
		371 [3]
$\text{C}_{18}\text{N}_{24}$	Type I clathrate	257.35
$\text{C}_{23}\text{N}_{23}$	Type I clathrate	311.6
$\text{Li}_8\text{C}_{23}\text{N}_{23}$	Type I clathrate	245.18
$\text{Si}_{23}\text{C}_{23}$	Type I clathrate	124.03
Si_6C_{40}	Type I clathrate	196.8
$\text{Si}_{18}\text{N}_{24}$	Type I clathrate	96.08
$\text{Si}_{23}\text{N}_{23}$	Type I clathrate	114.13
C_6Si_{40}	Type I clathrate	62.9
C (Diamond)	Diamond cubic	438.8 [15]
		442* [16]
$\alpha\text{-C}_3\text{N}_4$	Hexagonal	378.7 [15]
$\beta\text{-C}_3\text{N}_4$	Cubic spinel	419.1 [15]
$\text{c-Si}_3\text{N}_4$	Cubic spinel	300 [17]
		300* [18]
SiC	Cubic (Zinc blend)	225* [19–21]

Note: Experimental values are indicated by an asterisk (*).

constant of selected intermetallic clathrate compounds. The CPMD code [11] is a plane wave implementation of the Density Functional Theory.[12] It uses an approximation frozen-core approach where only the chemically active valence electrons are dealt with explicitly and the inert core electrons are considered frozen together with the nuclei as rigid non-polarizable ion cores. It is capable of both first-principles wave function optimization (static calculation) and *ab initio* molecular dynamics calculations. The PBE functional [22] and projector-augmented wave [23,24] potentials were used along with the plane wave basis sets for the geometry optimization and self-consistent total energy calculations. The energy cutoff for the plane wave basis set was 2,041 eV. The convergence energy criterion was set to be 3×10^{-5} eV. Reciprocal space was sampled using $3 \times 3 \times 3$ Monkhorst Pack meshes centered at Gamma. The number of k -point was 64 ($4 \times 4 \times 4$). For crystalline solids, the energy and equilibrium lattice constant of a unit cell at ground state (0 K) were computed by calculating the energies for unit cells with different lattice constants by performing wave function optimization with CPMD. A high-order (e.g. 4th order) polynomial was fitted to the energy points. The equilibrium lattice constant was determined by finding the lattice constant corresponding to the minimum energy on the polynomial curve. The formation energies were calculated by subtracting the total energies of the elements from the energy of the structure, then dividing

by the total number of atoms. For example, the formation energy, ΔE_{form} , for $A_xN_yC_{46-y-z}\square_z$ was calculated using the equation given by

$$\Delta E_{\text{form}} = \frac{E(A_xN_yC_{46-y-z}\square_z) - xE(A) - yE(N) - (46 - y - z)E(C)}{x + 46 - z}, \quad (2)$$

where $E(N)$, $E(C)$, and $E(A)$ are the energies per atom for nitrogen, C (diamond), and A metal, respectively. Similarly, the same approach was utilized to compute the energy of formation for $A_xN_ySi_{46-y}$ by replacing C with Si for all pertinent energy parameters.

Synthesis Method Table 2 provides a list of the candidate series and the elemental or alloy components constituting the admixture of starting materials. Magnesium powder (>99.87%, 32 mesh) was obtained from Noah Technology (San Antonio, TX). Barium (99.2%, < 0.8 % Sr, in pieces) was purchased from Alfa Aesar (Ward Hill, MA) and graphitic carbon nitride powders (99.5%, 730 μm) were obtained from Carbodeon, Ltd. (Vantaa, Finland). The targeted compositions were mixed together inside an argon-filled glove box at the appropriate stoichiometric ratios as indicated in Table 3, each admixed composition was individually packaged in a stainless steel tubular container and sealed with Swagelok fittings before removing it from the argon-filled glove box. Both packaged compositions were then shipped to Sophisticated Alloys, Inc. (Butler, PA) for vacuum arc-melting in an industrial vacuum arc-melter. The arc-melting process was conducted in an argon atmosphere under a sub-atmospheric pressure.

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