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

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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 clathrate 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 C\textsubscript{3}N\textsubscript{4}, Si\textsubscript{3}N\textsubscript{4}, 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 C\textsubscript{20}, C\textsubscript{24}, and C\textsubscript{28} cages linked through SP\textsuperscript{3}-covalent bonds. Theoretical computations have shown that both Type I carbon clathrate (C\textsubscript{46}) and Type II carbon clathrate (C\textsubscript{136}) may exist as metastable phases under high pressures.\textsuperscript{[1–3]} Like silicon clathrates (Si\textsubscript{46}),\textsuperscript{[4,5]} Type I carbon clathrates, C\textsubscript{46}, is predicted to exist in a simple cubic structure that belongs to the space group \textit{Pm\textbar3}n, Number 223, and exhibits a lattice parameter of 6.696 Å.\textsuperscript{[3]} The cage structure of Type I carbon clathrate (C\textsubscript{46}) 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.\textsuperscript{[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.\textsuperscript{[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\textsubscript{x}X\textsubscript{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\textsubscript{x}M\textsubscript{y}X\textsubscript{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\textsubscript{x}M\textsubscript{y}X\textsubscript{46–y–z}\textsuperscript{□}, for non-stoichiometric compounds, where \textsuperscript{□} represents a vacancy and z is the number of vacancies on the framework. For simplicity, A\textsubscript{x}C\textsubscript{y}X\textsubscript{46–y} is used in this paper to signify both stoichiometric and 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\textsubscript{x}C\textsubscript{y}Si\textsubscript{46–y}) has been investigated theoretically by Chan et al.\textsuperscript{[10]} The energy of formation of A\textsubscript{x}C\textsubscript{y}Si\textsubscript{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 (Ba\textsubscript{9}C\textsubscript{6}Si\textsubscript{40}, Ba\textsubscript{49}C\textsubscript{20}Si\textsubscript{26}, and Ba\textsubscript{3}C\textsubscript{23}Si\textsubscript{23}), which were predicted to exhibit small positive energies of formation, were successfully synthesized utilizing a vacuum arc-melting technique.\textsuperscript{[10]} One implication of the findings of this investigation is that the carbon or silicon...
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 C46 framework and some of the Si atoms on the Si46 framework with N atoms, respectively. First-principles computational studies using the Car–Perrinello Molecular Dynamics (CPMD) code [11,12] indicate that the carbon atoms in the C46 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 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
insertion reduces the energy of formation to negative values, which indicates that Li\(_{x}N_{y}C_{46-y}\)-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 N\(_{x}\)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 A\(_{x}\)N\(_{y}\)C\(_{46-y}\), as shown in 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\(_{3}N_{4}\)-like compound with Li guest atoms. The values of the energy of formation for N\(_{x}\)Si\(_{46-y}\) are compared against those of C\(_{46}\), Si\(_{46}\), and Li\(_{x}N_{y}C_{46-y}\), in Figure 3. For the compositions considered, the N\(_{y}\)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 A\(_{x}\)N\(_{y}\)C\(_{46-y}\) and A\(_{x}\)N\(_{y}\)Si\(_{46-y}\), against those of C\(_{46}\), Si\(_{46}\), and A\(_{x}\)C\(_{y}\)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 (N\(_{x}\)C\(_{46-y}\)) and with guest atoms (A\(_{x}\)N\(_{y}\)C\(_{46-y}\)) and (2) N-substituted silicon clathrates without (N\(_{y}\)Si\(_{46-y}\)) and with guest atoms (A\(_{x}\)N\(_{y}\)Si\(_{46-y}\)).

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      | -2.000           |
| C\(_{18}N_{24}\)  | 6.8622      | -1.377           |
| C\(_{19}N_{27}\)  | 6.8148      | -1.803           |
| C\(_{20}N_{26}\)  | 6.8502      | -3.146           |
| C\(_{23}N_{33}\)  | 6.6596      | -2.5             |
| Li\(_2\)C\(_{18}N_{24}\) | 7.3192     | -2.742           |
| Li\(_3\)C\(_{18}N_{34}\) | 7.3336     | -3.051           |
| Li\(_4\)C\(_{23}N_{23}\) | 7.2716     | -0.578           |
| Li\(_{12}\)C\(_{18}N_{24}\) | 8.1592     | -5.765           |
| Li\(_{12}\)C\(_{18}N_{24}\) | 8.6003     | -6.192           |
| Li\(_4\)Si\(_{18}N_{24}\) | 9.3206     | -4.832           |
| Si\(_{46}\)       | 10.238      | -0.571           |
| Si\(_{18}N_{24}\) | 9.0215      | -6.338           |
| Si\(_{23}N_{23}\) | 9.0546      | -5.417           |
| Li\(_{12}\)Si\(_{18}N_{24}\) | 9.8924     | -6.092           |

Figure 3. A comparison of the energy of formation for C\(_{46}\), N\(_{x}\)C\(_{46-y}\), Li\(_{x}N_{y}C_{46-y}\), Si\(_{46}\), N\(_{y}\)Si\(_{46-y}\), and Li\(_{x}N_{y}Si_{46-y}\) as a function of lattice parameter.

Figure 4. A comparison of the energy of formation for A\(_{x}\)C\(_{y}\)Si\(_{46-y}\), A\(_{x}\)N\(_{y}\)C\(_{46-y}\), and A\(_{x}\)N\(_{y}\)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 A\(_{x}\)C\(_{y}\)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 (N\(_{x}\)C\(_{46-y}\)) and with guest atoms (A\(_{x}\)N\(_{y}\)Si\(_{46-y}\)) 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 (Ba\(_{x}\)C\(_{y}\)Si\(_{46-y}\), Ba\(_{x}\)C\(_{y}\)Si\(_{46-y}\), and Ba\(_{x}\)C\(_{y}\)Si\(_{46-y}\)) 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 A\(_{x}\)C\(_{y}\)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 N\(_{x}\)C\(_{y}\)Si\(_{46-y}\), 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) | Total (g/mol) | Estimated density (g/cc) |
|-------------|----------------------------|----------|---------------|--------------------------|
| 1           | Mg₈C₁₈N₂₄                  |          |               |                          |
|             |                            | 3.51     | 17.4          | 2.34                     |
|             |                             | 137.327  | 24.305        | 40.0962                  |
| 2           | Ba₈C₁₈N₂₄                  | 8        | 6             |                          |
|             |                            | 1.74     | 240.58        | 435.02                   |
|             |                             | 25.00    | 12.08         |                          |
|             | Ba₈C₁₈N₂₄                  | 0.00     | 0.0           | 20/60 11.17              |
|             | Mg₈C₁₈N₂₄                  | 194.44   | 240.58        | 13.83                     |
|             |                             | 1,098.62 | 0.0           | 25.11                     |
|             |                             | 0.0      | 4.51          | 7.61                      |
|             |                             | 25.11    |               |                          |
|             |                             | 7.61     |               |                          |

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

| Composition | Target compound | Actual compounds produced | Type I clathrate |
|-------------|-----------------|----------------------------|------------------|
| 1           | Mg₈N₁₈C₂₈      | MgO, g-C₃N₄, and MgCN₂     | No               |
| 2           | Ba₈N₁₈C₂₄      | Ba, g-C₃N₄, and Ba₈C₁₈N₂₄ | Yes (Ba₈C₁₈N₂₄) |

A inside the cage structure wherein the composition of this series of Type I clathrates is qualitatively represented by the formula AₓNₙC₂₅Si₄₅₋ₙ₋ₓ₋ₙ, with 1 ≤ y ≤ 44 and 1 ≤ z ≤ 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 BaₙNₙC₁₄Si₂₃, BaₙNₙC₁₀Si₂₅, BaₙNₙC₁₆Si₂₈, BaₙNₙC₁₄Si₂₄, LiₙNₙC₁₀Si₂₃, LiₙNₙC₁₄Si₂₃, LiₙNₙC₁₀Si₂₅, LiₙNₙC₁₄Si₂₄, 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-C₃N₄ + xH_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 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 g-C₃N₄+xH_y as the starting materials. Admixtures of Ba and g-C₃N₄+xH_y (in the proportion of 20.6 g Ba and 4.51 g of g-C₃N₄+xH_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 g-C$_3$N$_4$+$H_2$ starting materials. However, the remaining reflections in the XRD spectra do not belong to Ba and g-C$_3$N$_4$+$H_2$, and some have been attributed to the Type I clathrate structure in question. The theoretically computed reflections for Ba$_8$C$_{18}$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 Ba$_8$C$_{18}$N$_{24}$ product. The crystal structure of this clathrate compound is close to those of Ba$_8$N$_{18}$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]

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

where $\Delta E/V$ is the energy change per unit cell volume, $B$ is the bulk modulus, and $\delta$ is the normal strain in the three principal directions of the unit cell. A plot of $\Delta E/V$ versus $\delta$ 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 and 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$\sim$N, N$\sim$Si, and C$\sim$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 $\beta$-C$_3$N$_4$, but are comparable to silicon nitride (C-Si$_3$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 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 $3 \times 10^{-5}$ 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

| Compound | Structure | $B$ (GPa) |
|----------|-----------|-----------|
| C$_{46}$ | Type I clathrate (Simple cubic) | 373.7 | 409 \[1\] |
| | | 363.7 \[2\] | 371 \[3\] |
| C$_{18}$N$_{24}$ | Type I clathrate | 257.35 |  |
| C$_{21}$N$_{23}$ | Type I clathrate | 311.6 |  |
| Li$_2$C$_{21}$N$_{23}$ | Type I clathrate | 245.18 |  |
| Si$_{23}$C$_{23}$ | Type I clathrate | 124.03 |  |
| Si$_6$C$_{40}$ | Type I clathrate | 196.8 |  |
| Si$_{18}$N$_{24}$ | Type I clathrate | 96.08 |  |
| Si$_{23}$N$_{23}$ | Type I clathrate | 114.13 |  |
| C$_6$Si$_{40}$ | Type I clathrate | 62.9 |  |
| C (Diamond) | Diamond cubic | 438.8 \[15\] | 442* \[16\] |
| $\alpha$-C$_3$N$_4$ | Hexagonal | 378.7 \[15\] |  |
| $\beta$-C$_3$N$_4$ | Cubic spinel | 419.1 \[15\] |  |
| c-Si$_3$N$_4$ | Cubic spinel | 300 \[17\] |  |
| SiC | Cubic (Zinc blend) | 225* \[19–21\] |  |
by the total number of atoms. For example, the formation energy, $\Delta E_{\text{form}}$, for $A_xN_yC_{46-y-z}\Box_z$ was calculated using the equation given by

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

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%, 30 µm) were obtained from CarboDecon, 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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**References**

[1] Perrottoni CA, da Jornada JAH. The carbon analogues of type-I silicon clathrates. J Phys: Condens Matter. 2001;13:5981–5998.

[2] Wang J-T, Chen C, Wang D-S, Mizuseki H, Kawazoe Y. Phase stability of carbon clathrates at high pressure. J Appl Phys. 2010;107:063507, 1–4.

[3] Rey N, Muñoz A, Rodríguez-Hernández P, San Miguel A. First-principles study of lithium-doped carbon clathrates under pressure. J Phys: Condens Matter. 2008;20:215218, 1–7.

[4] Adams, GB, O’Keeffe M, Kemkow AA, Sankey OF, Huang Y-M. Wide-band-gap Si in opine four-fold-coordinated clathrate structures. Phys Rev B. 1994;49: 8084–8053.

[5] Melinon P, Kehgelian P, Perez A, Champignon B, Guyot Y, Savioz L, Rege C, Pouchard M, Dianoux AJ. Phonon density of states of silicon clathrates: characteristic width narrowing effect with respect to the diamond phase. Phys Rev B. 1999;59: 10099–10103.

[6] Rogl P. Intermetallic clathrates: a challenge for thermoelectric. Austria: Institute of Physical Chemistry, University of Vienna; 2006.

[7] San-Miguel A, Toulemonde P. High-pressure properties of group IV clathrates. High Press Res. 2005;25(3):159–185.

[8] Cros C, Pouchard M. The clathrate phases of silicon and related elements (C, Ge, Sn): a historical approach. C R Chim. 2009;12:1014–1056.

[9] Nolas GS, Schumman SB, Slack GA. Chapter 6, Semiconductor clathrusters: a phonon glass electron crystal material with potential for thermoelectric applications. In: Tritt TM, editor. Semiconductors and semimetals. Vol 69. San Diego: Academic Press; 2001. p. 255–300.

[10] Chan KS, Miller MA, Liang W, Ellis-Terrell C, Peng X. First-principles computational design and synthesis of hybrid carbon-silicon clathrates. J Mater Sci. 2013.

[11] Car R, Parrinello M. Molecular dynamics: an ab initio electronic structure and molecular dynamics program. Version 3.13.1. The CPMD consortium; Stuttgart: IBM and Max Planck Institute. 2008 [cited 2008 Jun 27]. Available from: http://www.cpmd.org.

[12] Car R, Parrinello M. Unified approach for molecular dynamics and density functional theory. Phys Rev Lett. 1985;55(22):2471–2474.

[13] Diamond Version 3.2. Crystal Impact. Bonn, Germany; 2013. Available from: http://www.crystalimpact.com

[14] Wang SQ, Ye HQ. Ab initio electronic constants for the lonsdaleite phases of C, Si and Ge. J Phys: Condens Mater. 2003;15:5307–5314.

[15] He J, Guo L, Guo X, Liu R, Tian Y, Wang H, Gao C. Predicting hardness of dense CSN4 polymorphs. Appl Phys Lett. 2006;88:101906–1–3.

[16] Teter DM. Computational alchemy: the search for new superhard materials. MRS Bull. 1998;23:22–27.

[17] He-H, Sekine T, Kobayashi T, Hiroskih H, Suzuki I. Shock-induced phase transition of β-Si3N4 to c-Si3N4. Phys Rev B. 2000;62:11412–11417.

[18] Jiang JZ, Lindov R, Gerward I, Stahl K, Rhee OJ, Mori-Sanchez P, Carlson J, Mezouar M, Dooyhee E, Fitch A, Frost DJ. Compressibility and thermal expansion of cubic silicon nitride. Phys Rev B. 2002;65:161302(R)-1–4.

[19] Carnahan RD. Computational properties of silicon carbide. J Am Ceram Soc. 1968;51:223–224.

[20] Yean DH, Ritter JR. Estimates of isostructural bulk moduli for group IVA crystals with the zinblende structure. J Phys Chem Solids. 1971;32:653–655.

[21] Aguado F, Baoza VG. Prediction of bulk modulus at high temperatures from longitudinal phonon frequencies: application to diamond, c-BN, and 3C-SiC. Phys Rev B. 2006;73:024111–1–5.

[22] Perdew P, Burke K, Ernzerhof M. Generalized gradient approximation made simple. Phys Rev Lett. 2006;77(18):3865–3868.

[23] Blochl PE. Projector augmented-wave method. Phys Rev B. 1994;50(24):17953–17979.

[24] Kresse G, Joubert D. From ultrasoft pseudopotentials to the project augmented-wave method. Phys Rev B. 1999;59(3):1758–1775.