**ABSTRACT**

Carbon clathrate materials, comprised of sp3 carbon structures with light elements, as well as polymeric carbon monoxide, represent two classes of high-pressure materials with promising potential structural and energetic applications. A systematic exploration of PTx space was performed in carbon+ alkali and alkaline earth metals, under high-pressure/temperature conditions, as well as silicon-based systems, to establish the propensity to for sp3-based carbon/silicon networks with superlative properties. For the case of silicon, it was unambiguously determined that silicon clathrates are thermodynamically stable at high-pressure conditions. This suggests that other high-pressure, synthesis, clathrate, poly-CO
Pressure-induced Formation of Energetic and Structural Extended Solids with Quench-recovery to Ambient Conditions

ABSTRACT

Carbon clathrate materials, comprised of sp3 carbon structures with light elements, as well as polymeric carbon monoxide, represent two classes of high-pressure materials with promising potential structural and energetic applications. A systematic exploration of PTx space was performed in carbon+ alkali and alkaline earth metals, under high-pressure/temperature conditions, as well as silicon-based systems, to establish the propensity to for sp3-based carbon/silicon networks with superlative properties. For the case of silicon, it was unambiguously determined that silicon clathrates are thermodynamically stable at high-pressure conditions. This suggests that other high-pressure phases may be synthesized outside their thermodynamic stability regime and elucidates the first example of the chemical synthesis of a high-pressure phase at ambient-pressure conditions. We examined the sodium removal from a newly discovered NaSi6 (Na4Si24) compound. Upon complete sodium removal, a new sp3 silicon allotrope was produced that possesses a quasidirect band gap with the ideal value for photovoltaic applications. For the case of carbon, mixtures with Li, Mg, Na, and Ca were investigated. All systems showed known carbide formation under certain conditions, but several new and recoverable phases were identified including Mg2C, Mg2C3, Ca2C, Ca2C3 and Ca3C2. Some of these, such as Mg2C, contain unusual anions like C4- that are recoverable to ambient conditions and display sp3 carbon hybridization. These may serve as useful precursors for carbon clathrate materials. The polymerization behavior of CO (poly-CO, p-CO) was examined over a range of conditions with different dopants. The presence of molecular nitrogen and acetylene did not significantly affect the polymerization pressure of CO or the molecular structure of the resulting polymer. The presence of amorphous carbon and SiO2 appear to reduce the polymerization pressure by a fraction of one GPa. The presence of metallic lithium and sodium appear to reduce the polymerization pressure substantially. These additives may be considered as a route to producing larger quantities of p-CO.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

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<td>Oleksandr O. Kurakevych, Timothy A. Strobel, Duck Young Kim, Takaki Muramatsu, Viktor V. Struzhkin. Na-Si Clathrates Are High-Pressure Phases: A Melt-Based Route to Control Stoichiometry and Properties, Crystal Growth &amp; Design, (01 2013): 0. doi: 10.1021/cg3017084</td>
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(b) Papers published in non-peer-reviewed journals (N/A for none)

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(c) Presentations

1) High Pressure Gordon Research Conference, Biddeford, ME, June 24-29, 2012

Number of Presentations: 6.00

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<td>DuckYoung Kim, Stevce Stefanoski, Olesandr O. Kurakevych, Timothy A. Strobel. A new allotrope of silicon with a quasidirect band gap, To be submitted for publication (08 2013)</td>
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**Awards**


(2) Mg2C publication (Angewandte Chemie) featured on inside back cover

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The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

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**Sub Contractors (DD882)**

**Inventions (DD882)**
Scientific Progress

We have investigated the high-pressure / high-temperature (HP / HT) synthesis of novel structural and energetic solids, based on carbon and oxygen-carbon frameworks, which are expected to exhibit exceptional materials properties, show ambient quench recoverability and have potential for larger-volume scaling. We have examined a broad range of PTx conditions in the carbon (silicon) + alkali or alkaline earth metal systems to determine the extent of HP compound formation, ambient recoverability and new materials properties. We have investigated the polymerization of carbon monoxide (p-CO) under HP conditions in the presence of dopants and catalytic additives to determine effect on polymerization onset pressure and chemical stability.

Summary of the most important results are enumerated below as concise conclusions, supporting discussion with tables & figures are provided in the attached document.

1) Sodium-silicon clathrates are HP phases. This indicates that HP phases may be synthesized through chemical precursors at ambient conditions.

2) A new structure, NaSi6, was discovered at HP. This phase is recoverable to ambient conditions and shows unusual, potentially quasi-one-dimensional, electrical resistivity.

3) By treating a NaSi6 precursor compound (Na4Si24 unit cell) we were able to produce a new pure allotrope of silicon (Si24) that has a quasidirect band gap.

4) Carbon + light metal systems show rich behavior under HP/HT conditions. Several previously unreported structures and compounds were discovered.

5) A new carbide, Mg2C, was discovered at HP/HT conditions. This phase is fully recoverable to ambient conditions. It has a bulk modulus of 87 GPa and is electrically insulating. This compound could potentially act as a solid-based fuel source as it is readily hydrolyzed to form CH4 gas.

6) The thermodynamic properties of Mg2C were established and the conditions of high-pressure, high-temperature stability have been determined.

7) A new polymorph of Mg2C3 carbide was discovered and the crystal structure was solved using a combination of experimental and theoretical methods.

8) New structures in the Ca+C system were identified. Some of these may contain unique polymeric carbon units.

9) Methods were developed to prepare samples of p-CO. This can be done routinely for samples with dimensions of 1000 micron diameter x 150 micron thickness.

10) The polymerization pressure of CO in the presence of N2 and C2H4 is not reduced from the pure CO sample conditions. These dopants tend to phase separate with no significant alteration of the chemical structure; however, subtle vdW-type interaction was observed.

11) Neither seed crystals of p-CO nor nano-sized Pd powder reduce the pressure required for CO polymerization at ambient temperature.

12) Amorphous carbon appears to reduce the polymerization onset pressure of CO by ~0.5 GPa when compared with the pure system. It is unclear whether this is a catalytic (nucleation) or thermodynamic (chemical stabilization) effect.

13) The polymerization pressure of CO was investigated in the presence of several different metal and non-metal catalysts. Metallic lithium and sodium, as well as non-metallic amorphous carbon and SiO2, appear to reduce the pressure needed for CO polymerization.

Technology Transfer
Final Report

Attachment: Discussion and figures

Proposal Number: 60587EGDRP
Agreement Number: W911NF1110300
Proposal Title: Pressure-induced Formation of Energetic and Structural Extended Solids with Quench-recovery to Ambient Conditions
Report Period Begin Date: 09/01/2012
Report Period End Date: 02/28/2014

T.A. Strobel, M. Somayazulu, R.J. Hemley, O.O. Kurakevych

Abstract
Carbon clathrate materials, comprised of sp³ carbon structures with light elements, as well as polymeric carbon monoxide, represent two classes of high-pressure materials with promising potential structural and energetic applications. A systematic exploration of PTx space was performed in carbon+ alkali and alkaline earth metals, under high-pressure/temperature conditions, as well as silicon-based systems, to establish the propensity to for sp³-based carbon/silicon networks with superlative properties. For the case of silicon, it was unambiguously determined that silicon clathrates are thermodynamically stable at high-pressure conditions. This suggests that other high-pressure phases may be synthesized outside their thermodynamic stability regime and elucidates the first example of the chemical synthesis of a high-pressure phase at ambient-pressure conditions. We examined the sodium removal from a newly discovered NaSi₆ (Na₄Si₂₄) compound. Upon complete sodium removal, a new sp³ silicon allotrope was produced that possesses a quasidirect band gap with the ideal value for photovoltaic applications. For the case of carbon, mixtures with Li, Mg, Na, and Ca were investigated. All systems showed known carbide formation under certain conditions, but several new and recoverable phases were identified including Mg₂C, Mg₂C₃, Ca₂C, Ca₂C₃ and Ca₃C₂. Some of these, such as Mg₂C, contain unusual anions like C⁴⁻ that are recoverable to ambient conditions and display sp³ carbon hybridization. These may serve as useful precursors for carbon clathrate materials. The polymerization behavior of CO (poly-CO, p-CO) was examined over a range of conditions with different dopants. The presence of molecular nitrogen and acetylene did not significantly affect the polymerization pressure of CO or the molecular structure of the resulting polymer. The presence of amorphous carbon and SiO₂ appear to reduce the polymerization pressure by a fraction of one GPa. The presence of metallic lithium and sodium appear to reduce the polymerization pressure substantially. These additives may be considered as a route to producing larger quantities of p-CO.

Scientific progress and accomplishments

1) Sodium-silicon clathrates are HP phases. This indicates that HP phases may be synthesized through chemical precursors at ambient conditions.

For the first time we have demonstrated unambiguously that Na+Si clathrates are thermodynamically stable high-pressure phases. Sodium clathrates were prepared from elemental Na/Si mixtures (20 at% of Na, i.e., ~5% excess as compared with stoichiometric sI and sII clathrates) using the multi-anvil press technique at pressures between 1-8 GPa and temperatures between 700-1275 K. Figure 1 shows the x-ray diffraction pattern obtained from a sample that was recovered from 6 GPa and 1100 K. The x-ray diffraction pattern indicates that
sl clathrate may be synthesized directly from the elements under HP/HT conditions. In addition we have performed DFT calculations that confirm the high-pressure thermodynamic stability.

![X-ray diffraction pattern of sl clathrate synthesized at 6 GPa and 1100K.](image)

**Figure 1.** (a) X-ray diffraction pattern of sl clathrate synthesized at 6 GPa and 1100K. (b) Images of metallic sl (Na₈Si₄₆), scale bar is 50 microns. (c) atomic structure of sl clathrate.

These results open new perspectives for high-pressure synthesis and properties control of new advanced materials. The high-pressure thermodynamic stability of Na-Si clathrate phases allows for a melt-based synthesis approach, which could be very useful for compositional control in mixed phases (e.g., Na+Ba etc.), high-quality single crystals, and for precise tuning of the occupancy ratios. All phases formed in this pressure domain allow for larger-volume scaling of materials (from 40 cm³ for cubic sl at ~3 GPa to 1 cm³ at ~8 GPa). Our results reveal the existence of multiple chemical mechanisms that allow for synthesis of high-pressure phases “without pressure”. Because the thermodynamic stability fields of Na-Si clathrate phases only exist under high-pressure conditions, previous reports of these structures may be viewed as non-equilibrium, precursor-based syntheses of high-pressure phases at low-pressure conditions. The understanding of such intrinsic interrelationships between thermodynamics and kinetics is thus the next step to explore that could open potential for other precursor-based synthesis of other high-pressure phases, especially carbon-based materials. Na-Si clathrate formation may be viewed as the first chemical example of a high-pressure phase at ambient conditions.

2) A new structure, NaSi₆, was discovered at HP. This phase is recoverable to ambient conditions and shows unusual, potentially quasi-one-dimensional, electrical resistivity.

During the synthesis of Na+Si clathrate phases, the formation of a novel Na-Si compound, NaSi₆ was observed when pressure was increased to 8 GPa. It has the Eu₄Ga₆Ge₁₆ structural type (Fig. 2), never reported thus far for an alkali metal. The structure is composed of sp³-bonded Si atoms, which form tunnels, intercalating Na atoms along the a-axis. As compared to BaSi₆, SrSi₆, and CaSi₆, the corresponding sodium compound forms at substantially lower pressure: 8 GPa as compared to 11.5 GPa and 10 GPa for BaSi₆ and CaSi₆, respectively. The pressure for NaSi₆ formation allows consideration of this phase for a large-volume production, e.g., in the toroid-type high-pressure systems, contrary to similar compounds of alkali-earth metals.
Figure 2. (a) X-ray diffraction pattern of NaSi₆ at 8 GPa and 1100K. (b) Images of metallic NaSi₆, scale bar is 50 microns. (c) Atomic structure of NaSi₆.

The electrical resistivity of NaSi₆ as a function of temperature was measured by the standard four-electrode technique, using a Physical Property Measurement System (PPMS: Quantum Design, Inc.). Overall, NaSi₆ exhibits metallic behavior, with the electrical resistivity increasing approximately as a parabolic curve with temperature above 75 K (Fig. 3). Below 75 K, the electrical resistivity begins to increase with further temperature decrease, a feature never observed so far for related compounds within this structural family. The observed minimum at about 75 K might be caused by the complexity of the electronic band structure, particularly the one-dimensional nature of the Na channels, or an unknown magnetic scattering process.

Figure 3. Electrical resistivity of NaSi₆ as a function of temperature. Inset shows the calculated band structure at 1 MPa.

3) By treating a NaSi₆ precursor compound (Na₄Si₂₄ unit cell) we were able to produce a new pure allotrope of silicon (Si₂₄) that has a quasidirect band gap.

Previously, we demonstrated unambiguously that Na+Si clathrates are thermodynamically stable high-pressure phases, and also reported the discovery of a new NaSi₆ (Na₄Si₂₄ unit cell) compound. This compound consists of a channel-like sp³ silicon host structure with chains of
sodium atoms as a guest structure. These open channels that host sodium atoms suggest a possible pathway for sodium removal via diffusion along the channels as schematically shown in Figure 4.

![Figure 4](image.png)

Figure 4. (a) Schematic of compositional changes from Na₄Si₂₄ (left) to Si₂₄ (right). Na atoms are shown in purple and silicon in yellow. (b) Si₂₄ unit cell exhibiting three crystallographically unique positions in each color (c) Fractional view of Si₂₄ emphasizing its channel structure. Channels are formed by eight-member rings along the a-axis, which are linked by six-membered rings on the top and sides. These channels are connected along the c-axis by five-membered rings.

By exposing the recovered Na₄Si₂₄ samples to elevated temperatures, removal of Na atoms from the structure was observed. This process occurs at temperatures as low as 320 K, while type-II silicon clathrates (Na₆Si136) require much higher temperatures (> 623 K) for Na removal. Thermal “degassing” of Na₄Si₂₄ at 400 K under dynamic vacuum conditions resulted in a gradual reduction of the sodium content and sodium was completely removed from the structure over a period of eight days. The structure of the resulting Na-free structure is unchanged (Cmcm), however, the lattice constants are slightly modified. We verified the absence of Na from the structure using powder X-ray diffraction and energy dispersive X-ray spectroscopy. No sodium was found within our instrumental detection limits (0.1 atom%), therefore, the new structure may be considered as a new allotrope of silicon.

We investigated the electronic and optical properties of the Si₂₄ allotrope using a combination of experimental and theoretical methods (Figure 5). The new structure possess a quasidirect bandgap of ~1.3 eV, which suggests that this structure will be a very useful optoelectronic material. The quasidirect band structure of Si₂₄ overcomes one of the most fundamental limitations of the “normal” diamond-structured silicon phase, which possesses an indirect band gap.
Figure 5. Electronic and optical properties of Si_{24}. (a) Calculated Si_{24} band structure (PBE). (b) Zoomed in region of band gap with table showing DFT (PBE) and G0W0 corrected values. Arrows indicate direct (Ed) and indirect (Ei) gaps. (c) Electrical conductivity of Na₄Si_{24} and Si_{24} (inset shows fit of intrinsic conductivity region with band gap of 1.3 eV). (d) Tauc plots of Kubelka-Munk absorption (K/S) for Si_{24} obtained from optical reflectivity measurements. Absorption edges are observed at 1.29 eV and 1.39 eV assuming indirect and direct transitions, respectively.

4) **Carbon + light metal systems show rich behavior under HP/HT conditions. Several previously unreported structures and compounds were discovered.**

The phase behavior and structural evolution of several carbon + light metal systems were investigated under HP/HT conditions. Sources of carbon have included glassy amorphous carbon, nano carbon and graphite, while lights metals have been limited to Li, Mg, Na, and Ca. Results are summarized as follows:

- Below 5 GPa the formation of Li₂C₂ (known carbide phase) was observed. Above 12 GPa, at least one new phase was discovered in the Li+C system. Figure 6 shows x-ray diffraction and Raman spectra obtained from this phase, which cannot be described by any known Li+C compounds. Raman modes observed near 1200 cm⁻¹ may be indicative of sp³-type carbon bonding. All of the phases determined thus far are recoverable to ambient conditions.
Up to 20 GPa, we have only observed the formation of the known carbide Na₂C₂ in the Na+C system.

Below 5 GPa the formation of CaC₂ (known carbide phase) was observed. Above 7 GPa several new phases were discovered (see below).

The Mg+C system was studied extensively – two new recoverable HP phases were discovered (see below).

5) A new carbide, Mg₂C, was discovered at HP/HT conditions. This phase is fully recoverable to ambient conditions. It has a bulk modulus of 87 GPa and is electrically insulating. This compound could potentially act as a solid-based fuel source as it is readily hydrolyzed to form CH₄ gas.

The Mg+C carbon was investigated over a broad range of synthesis conditions: 7-70 mol% Mg, 1-30 GPa and 500-2000 K. Various sources of carbon have been tested, including glassy amorphous carbon, nano carbon and graphite. At the composition 66 mol% Mg and pressure above 15 GPa, the formation of nearly phase-pure Mg₂C was discovered. Figure 6 shows an xrd pattern obtained from a synthesis run recovered from 15 GPa and ~1700 K and the corresponding Mg₂C structure. Confirmation of the [C⁺] methanide ion was performed by hydrolyzing samples, which produced CH₄ gas.

Figure 7 shows the crystal structure of Mg₂C and structural coordination. Carbon within Mg₂C is 8-fold coordinated by magnesium, whereas carbon coordination within Mg₂C₃ and MgC₂ is much more sophisticated. If one considers the whole carbon anions as structural units, Mg₂C₃ and Mg₂C have the same coordination number 8, but in the first case they form a distorted and elongated dodecahedron, while in the second case the coordination polyhedron is a regular
cube. In MgC₂, the C₂ dumbbell coordination number is 6 (elongated octahedron). Contrary to Mg₂C₃ and MgC₂, Mg₂C does not contain covalent C-C bonds. Rather, carbon exists in a very unusual C⁺ ionic state.

The $^{13}$C NMR spectrum (Fig. 7c) of Mg$_2^{13}$C sample (99% of isotopic purity) displays one resonance at δ+102 ppm. This agrees with the antifluorite structure which contains only one unique crystallographic position for carbon. The chemical shift is significantly higher than that of C⁺ in Al₄C₃ (34 and 51 ppm for C atoms in two crystallographically different sites), and agrees well with higher degree of covalent character of Al-C bonding as compared with Mg-C. The absence of J-coupling in the observed NMR spectrum suggests that carbon within the compound is primarily ionic; increased covalency would be manifested by the presence of J-coupling.

Figure 7. (a) X-ray diffraction data with Mo K radiation (points), Rietveld refinement (line), difference (lower line). Tick marks are shown for Mg₂C (top) and MgO impurity (bottom). (b) Carbon and magnesium coordination in Mg₂C. (c) NMR spectrum of Mg₂¹³C (99% of isotope purity).

To gain further insights into the ionic chemical bonding, we calculated the electron density in the structure and performed a Bader-type bonding analysis (Fig. 8). These results confirm the highly ionic nature of the solid: the effective charges on Mg and C are +1.57 and -3.14, respectively. To our knowledge, this is the most negative effective charge of carbon ever achieved, while the C⁺ ionic radius in Mg₂C has the highest value of 1.50 Å. The magnesium charge is the lowest among other known carbides (+1.65 and +1.7 for Mg₂C₃ and MgC₂, respectively). The charge density in the (110) plane shows a nearly spherical distribution of electrons centered at Mg and C ions with a low electron density in the interstitial regions (Fig. 8a). The electron localization function (ELF, Fig. 8b) provides a closer look at the bonding nature. ELF minima observed between Mg and C atoms confirm the closed-shell ionic nature of the bonding. There is no "shared-electron" picture, which is characteristic of covalent bonding and requires ELF maxima between atoms.
The C⁺ character of this compound is very interesting. Although ionic, this carbon exists in an sp³ hybridized state and is stable at ambient conditions. We speculate that Mg₂C will serve as a very valuable precursor for the formation of diamond-like sp³ carbon at reduced pressure conditions. A direct analogy may be drawn between Mg₂C and Zintl precursors like Na₄Si₄, which are known to form sp³ clathrate structures at ambient pressure upon thermal decomposition (despite the fact that the clathrates are only thermodynamically stable at high pressure).

6) The thermodynamic properties of Mg₂C were established and the conditions of high-pressure, high-temperature stability have been determined.

The high-pressure and high-temperature stability of antifluorite Mg₂C was studied by using in situ X-ray diffraction up to 20 GPa and 1550 K. A combination of ab initio calculations of relative energies and phonon density of states as a function of pressure insights to the formation of Mg₂C under extreme conditions and ability to recoverability it at ambient conditions. Our results indicate that high pressure is a crucial point for the thermodynamic stabilization of C⁺ anion in the antifluorite structure, although this anion is fully recoverable to ambient conditions.

Figure 9 shows a sequence of in situ X-ray powder diffraction patterns of Mg-C sample, taken during compression to 18 GPa (at 300 K), with heating to 1550 K (at ~18 GPa) and subsequent isothermal decompression (at ~1550 K). The formation of Mg₂C was observed during heating at 18 GPa after the non-equilibrium melting of Mg at ~1500 K. At 1550 K Mg₂C decomposes at the pressure of ~ 12 GPa. A constant composition section (33 at.% C) of the p-T phase diagram of Mg₂C was established using our in situ data at 1550 K and the 0 K value predicted by ab initio calculations (stability compared to Mg-diamond mixture). The melting temperatures of Mg₂C at 1 MPa and 15 GPa were then estimated using a Lindemann mode combined with ab initio calculations of the Debye temperature under pressure and experimental p-V equation of state.
Figure 9. Experimental X-ray diffraction data obtained in situ during the HPHT formation of Mg₂C (left). Structures of graphite, Mg₂C, and diamond (center). Phase diagram determined for Mg₂C (right).

7) A new polymorph of Mg₂C₃ carbide was discovered and the crystal structure was solved using a combination of experimental and theoretical methods.

High-pressure, high-temperature studies were conducted in the Mg+C system at compositions other than Mg₂C, namely, Mg₂C₃. In this case, another structure was identified with a much more complex structure than cubic Mg₂C. With the assistance of ab initio structure searching methods, we were able to successfully solve the structure (Figure 10) from in situ X-ray data. Like the previously known orthorhombic Pnmm structure (α-Mg₂C₃), the new monoclinic C2/m structure (β-Mg₂C₃) contains linear C₃⁺ chains that are isoelectronic with CO₂. Unlike α-Mg₂C₃, which contains alternating layers of C₃⁺ chains oriented in opposite directions, all C₃⁺ chains within β-Mg₂C₃ are nearly aligned along the crystallographic c-axis. Hydrolysis of β-Mg₂C₃ yields C₃H₄, as detected by mass spectrometry, while Raman and NMR measurements show clear C=C stretching near 1200 cm⁻¹ and ¹³C resonances confirming the presence of the rare allylenide anion.

Figure 10. In situ angular dispersive diffraction pattern for β-Mg₂C₃ synthesized in the PE press and recovered to ambient pressure. Rietveld refinement was employed for the β-Mg₂C₃ structure, while Le Bail analysis was used for MgO and Mg due to strong preferred orientation.
caused by recrystallization and capsule texture. Tick marks indicate \( \beta\)-Mg\(_2\)C\(_3\), Mg and MgO from top to bottom.

The new Mg\(_2\)C\(_3\) structure is monoclinic with space group C2/m with \( a = 4.8 \), \( b = 4.7 \), \( c = 6.0 \) Å and \( b = 126^\circ \). This phase forms above \( \sim 6 \) GPa and is stable to \( \sim 15 \) GPa. Observations suggest that this structure transforms to Mg\(_2\)C at higher pressure (with heating and depending on global composition). Unlike Mg\(_2\)C, Mg\(_2\)C\(_3\) contains linear C\(_{34}^+\) chains that are charge balanced by Mg\(^{2+}\) cations (Fig. 11).

![New Mg\(_2\)C\(_3\) structure](image)

Figure 11. C\(_{34}^+\) coordination in \( \alpha \) and \( \beta \) Mg\(_2\)C\(_3\) and histogram of nearest neighbor Mg-C distances out to 3 Å.

8) New structures in the Ca+C system were identified. Some of these may contain unique polymeric carbon units.

Studies were performed in the Ca+C system to investigate the influence of Ca on sp\(^3\) carbon network formation. At pressures <4 GPa, we observed the formation of CaC\(_2\) calcium carbide, a known structure with linear C\(_2^2-\) dumbbells. At higher pressure, new structures were identified. Figure 12 shows in situ X-ray diffraction patterns obtained at 20 GPa and 600-900 K. The starting FCC (or BCC depending on pressure) metal clearly transforms into a lower symmetry structure(s).
Figure 12. X-ray diffraction patterns obtained for Ca+C mixtures at 20 GPa heated to 600 K (bottom) and 900 K (top). Low symmetry structures are clearly identified.

With the aid of ab initio structural searching, we have identified candidate structures for the new Ca+C compounds. Figure 13 shows possible structure and corresponding XRD patterns that match closest to the experimental data. Both of these structures (P-1 and Immm symmetries) contain 1D carbon nano chains.

Figure 13. Simulated X-ray diffraction patterns and crystal structures for new CaC₂ compounds with P-1 symmetry (top) and Immm symmetry (bottom).

These structures are very unique in the sense that they contain polymerized carbon nano-ribbons. These phases should be metallic with very interesting properties. Furthermore, they offer the possibility of extracting 1D carbon nanochains, which may have very interesting mechanical properties.
In addition to this, we have identified three new carbide structures up to 30 GPa, using a combination of X-ray diffraction methods and *ab initio* crystal structure searching (Fig. 14). Ca$_2$C contains C$^+$ anions, similar to Mg$_2$C, however, the structure is orthorhombic. Monoclinic Ca$_2$C$_3$ is isostructural with β-Mg$_2$C$_3$, but no a modification is known for the case of Ca. Finally, an entirely new composition, Ca$_3$C$_2$, was discovered. This structure is metallic and does not have formal charge balance.

![Structures and X-ray diffraction patterns for new Ca-C carbides.](image)

9) **Methods were developed to prepare samples of p-CO. This can be done routinely for samples with dimensions of 1000 micron diameter x 150 micron thickness.**

We have developed experimental procedures to load CO into diamond anvil cells (DAC) using both cryogenic and high-pressure gas methods. These techniques are extremely reliable (near 100% loading efficiency). When utilizing the supported anvil design (Boehler-Almax style), large samples may be produced (1000 micron diameter x 150 micron thickness at 7 GPa).
10) The polymerization pressure of CO in the presence of N₂ and C₂H₄ is not reduced from the pure CO sample conditions. These dopants tend to phase separate with no significant alteration of the chemical structure; however, subtle vdW-type interaction was observed.

Experiments were conducted on mixtures of CO and N₂ or C₂H₄ to determine if polymerization in the presence of these compounds would decrease the polymerization onset pressure or increase the chemical stability through bonding with the p-CO network. Neither of the components was found to reduce the polymerization pressure required for pure CO (~6 GPa at room temperature). Both N₂ and C₂H₄ exhibited phase separation from p-CO and infrared (IR) spectra obtained from the different samples did not indicate any significant bonding changes in the polymer structure. However, subtle shifts in Raman modes suggest the presence of weak van der Waals interaction. Figure 15 shows images of p-CO with N₂ and C₂H₄, as well as the corresponding IR spectra.

![Image of N₂+p-CO mixture and C₂H₄+p-CO mixture showing phase separation of the components. (c) IR spectra for the different samples indicating no significant changes in chemical bonding. For the case of C₂H₄, new IR modes appear which originate from pure C₂H₄.](image1)

11) Neither seed crystals of p-CO nor nano-sized Pd powder reduce the pressure required for CO polymerization at ambient temperature.

In order to reduce the polymerization onset pressure for pure CO, attempts were made to catalytically induce (reduce nucleation barrier) p-CO formation using nano-Pd powder and a seed crystal of pure p-CO. Neither of these additives was found to reduce the polymerization onset pressure. Figure 16 shows the seed crystal of p-CO surrounded by molecular CO and corresponding IR spectra.
Figure 16. Image of p-CO seed crystal inside diamond anvil cell at 5.9 GPa surrounded by molecular CO. The molecular CO does not polymerize, while in contact with the seed. IR spectra are shown at bottom.

12) Amorphous carbon appears to reduce the polymerization onset pressure of CO by ~0.5 GPa when compared with the pure system. It is unclear whether this is a catalytic (nucleation) or thermodynamic (chemical stabilization) effect.

The polymerization of CO was investigated in the presence of amorphous nano-carbon. Compared with pure CO, which always shows a polymerization onset pressure between 5.5-7 GPa depending on the exact experimental conditions, the sample in contact with nano carbon started to polymerize at only 4.8 GPa. This represents an approximate 0.5 GPa decrease in the pressure required for CO polymerization in the pure system. Figure 17 shows an image of the CO in contact with nano carbon and the corresponding IR spectra with pressure. It is unclear whether this process is catalytic in nature or if the carbon plays a chemically stabilizing role. The detailed determination of chemical stability is currently under investigation.
The polymerization pressure of CO was investigated in the presence of several different metal and non-metal catalysts. Metallic lithium and sodium, as well as non-metallic amorphous carbon and SiO₂, appear to reduce the pressure needed for CO polymerization.

We have used a combination of IR and Raman spectroscopy studies to explore the possibility of lowering the polymerization pressure of CO. We undertook three separate routes to systematically explore the lowering of polymerization pressure in CO. In the first study, we attempted to use the fact that several groups that have used diamond anvil cells reported a range of pressures depending on the gasket material. We hypothesized that this could indicate metal-CO interaction and therefore a dependence of this interaction on the polymerization pressure.

We chose to standardize the protocol by using Au lined stainless steel gaskets and IR spectrometry using the pressure shift of the antisymmetric NO₂ stretch as a pressure sensor and the appearance of carbonyl bands (at 720 cm⁻¹) and the epoxy bands (at 830 cm⁻¹). This was necessary to reduce the effect of photo-reactivity and also establish the formation of the correct polymeric phase. To strengthen the signal from the sample and proper referencing, we used gaskets with dual holes, one filled with the KNO₂-KBr mixture and the other completely filled with CO. The gasket geometry was first calibrated using ruby and N₂ in the sample chamber instead of CO.

Once this protocol was established, we used several metal additives such as nano-Pd, Pt, Pt-black, Al, Na, Li as well as common gasket materials such as Re, W, Fe and Cu. We also tested non-metallic additives of amorphous carbon and SiO₂ (Fig. 18).

Figure 18. The panel on the left shows CO loaded along with Pd sponge and the panel on the right shows CO with Na dispersed in the sample chamber. Both the samples were photographed at low pressures prior to polymerization. The gasket material used in both cases is Be-Cu.
Interaction between CO and non-metals such as C and SiO2 but with large surface area of contact such as glassy, nano-carbon, silica wool, carbon nanotubes

While no appreciable decrease in polymerization pressure or changes in the spectroscopic characteristics of the polymeric phase were observed in most cases, a modest reduction in the polymerization pressure was observed for amorphous carbon and SiO2. These studies have consistently shown reduction of polymerization pressure by at ~1 GPa and the resultant polymeric phase shows all the signatures reported previously.

A appreciable drop in polymerization pressure was also observed in the case of Li when mediated by slight increase in temperature. While in the case of Li, the polymerization pressure dropped to 1 GPa, in the case of Na, it dropped to 2 GPa when mediated with photo-reactivity of incident 532 nm or 488 nm laser radiation. When the experiment was repeated using 660 nm radiation, no change in polymerization pressure was observed.

X-ray diffraction of the polymerized products revealed a majority polymeric phase admixed with a small amount of crystalline phase that was not pure Na or Li indicative of a chemical reaction (Fig. 19). This could imply that the polymerization is indeed aided by interaction between the alkali metals and CO and further that the activation energy involved could be lowered either by increasing the surface of contact or temperature (photo-induced).

![Figure 19. The integrated diffraction patterns of the polymeric phase obtained with Li at 1 GPa and Na at 2.8 GPa. The broad peak weak signal is detected in both from the amorphous polymer. For Li, a crystalline phase was observed, which indicates a complicated large unit cell structure not similar to Li at this pressure (1.2 GPa).](image-url)