Synthesis of new cubic C₃N₄ and diamond-like BC₃ phases under high pressure and high temperature

P V Zinin¹, L C Ming¹, S K Sharma¹, S M Hong², Y Xie³, T Irifune⁴, T Shinmei⁴

¹Hawaii Institute of Geophysics & Planetology, University of Hawaii, Honolulu, HI 96822, U.S.A
²High Pressure Laboratory, Southwest Jiaotung University, Chengdu, Sichuan, China
³Department of Chemistry, University of Science and Technology of China, Hefei, Anhui, China
⁴Geodynamics Research Center, Ehime University, Matsuyama, 790-8577, Japan

E-mail: zinin@soest.hawaii.edu

Abstract. In this report, we discuss the progress in synthesis of new binary phases from B-C-N triangle in DAC under high-pressure and high-temperature (HPHT) conditions: cubic C₃N₄ (c-C₃N₄) and diamond-like BC₃ (d-BC₃) phase. These two phases have been synthesized by direct transformation from graphitic phases under HPHT conditions. The c-C₃N₄ phase was recovered at ambient conditions from the graphite-like C₃N₄ (g-C₃N₄) phase subjected to pressures between 21 and 38 GPa in a diamond anvil cell, laser-heated to temperatures between 1600 and 3000 K. The x-ray diffraction data on the new phase are best explained by a cubic unit cell with the lattice parameters $a = 3.878\pm0.001$ Å. The synthesis of the c-C₃N₄ phase has been also conducted in a large volume press at pressure 25 GPa and temperature 2000 °C. X-ray peaks of c-C₃N₄ phase obtained in the large-volume press are weaker than those of diamonds. Application of the UV Raman spectroscopy revealed that UV Raman spectrum of the g-C₃N₄ is substantially different from that measured with visible Raman spectroscopy. It has two strong peaks at 690 cm⁻¹ and at 986 cm⁻¹ assigned to different types of the ring (s-triazine ring) breathing modes. A diamond-like BC₃ has been synthesized at temperature 2033 ± 241 K and at pressure 50 GPa. The conclusion about the phase transition from graphitic BC₃ (g-BC₃) to d-BC₃ phase was made from the analysis of Raman scattering data. The Raman spectrum of the novel d-BC₃ displays all the peaks but one at 671 cm⁻¹ characteristic to Raman spectra the B doped diamond. The peaks pattern of the d-BC₃ suggests that this phase could become a superconductor at low temperatures.

1. Introduction
For nearly seventeen years, intense interest in the synthesis of new C-N materials has been generated by predictions of the unusual properties of saturated, i.e. $sp^3$-hybridized, crystalline C₃N₄-phases [1]. A search for the superhard phases led to successful synthesis of ternary cubic BC₂N phase in a diamond anvil cell (DAC) [2] and in large volume press [3]. Synthesis of the binary phases from the B-C-N triangle are of interest for two reasons: (a) binary phases could be harder than BC₂N; (b) for industrial applications their synthesis is expected to be less complex than that of the ternary BC₂N phase,
because additional elements in the compounds introduce additional difficulties in the synthesis of new phase(s) and in the development of the thin film deposition process. In this report, we discuss the progress in synthesis of new binary cubic phases from B-C-N triangle in DAC under high-pressure and high-temperature (HPHT) conditions: cubic \(\text{C}_3\text{N}_4\) [4] and diamond-like \(\text{BC}_3\) phases. We also provide evidence that the new \(c\)-\(\text{C}_3\text{N}_4\) phase can be synthesized not only in the DAC but also in a large volume press.

2. Synthesis of the cubic \(\text{C}_3\text{N}_4\) phase

The criterion for identification of the new phase can be found elsewhere [5]. It states: “The rules of synthetic chemistry are rigorous: to claim a new phase all diffraction lines of a given crystal phase should be present and the chemical composition should be \(\text{C/N}=3/4\)”. There are a number of publications whose authors claimed synthesis of new \(\text{C}_3\text{N}_4\) phases; however, their publications did not contain either x-ray diffraction (XRD) data or data on elemental compositions of the new phases [6]. Badzian et al. attributed the lack of success in synthesis of hypothetical superhard \(\text{C}_3\text{N}_4\) phase to the limitations in accuracy of first principle calculations, such as pseudopotential and total energy methods [5]. Indeed, a search for the superhard \(\text{C}_3\text{N}_4\) phase raises the fundamental question regarding the limitations in the application of the modern theoretical approaches for predicting new materials.

Our analysis of the available experimental data on the synthesis of the superhard carbon nitride indicates that it is premature to make a negative conclusion regarding the existence of the superhard \(\text{C}_3\text{N}_4\) phase. Examination of the literature on synthesis of carbon nitride reveals that the majority of experiments were conducted using thin film deposition techniques [6], and there are only few of publications on the high-pressure synthesis of \(\text{C}_3\text{N}_4\) phases [7]. Wixom was probably the first who used high-pressure, high-temperature (HPHT) conditions to synthesize \(\text{C}_3\text{N}\) by shock wave compression of a pyrolyzed melamine-formaldehyde resin and a tetrazol derivative [8]. Diamond was the only detectable crystalline phase in the product. A recent shock recovery experiments also showed that a new carbon nitride phase (“phase-X”) was formed at pressures to 50 GPa from nitrogen-rich precursors, amorphous C-N-O and dicyanodiamide [9]. Others approaches in synthesis of new \(\text{C}_3\text{N}_4\) phases under HPHT conditions used different precursors/compounds as the starting materials, including (a) pyrolyzing \(\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_4\text{S}\) in a nitrogen atmosphere [10], (b) laser-heating in a diamond anvil cell (LDAC) of the tetracyanoethylene (TCNE: \(\text{C}_6\text{N}_4\)) to 2500°C at 20 and 42 GPa [11]; (c) \(\text{C}_{60}\) particles with a nitrogen pressure medium, at temperatures ranging from approximately 100 to 5000 K and pressures of 10–60 GPa [12] in LDAC, (d) high-energy ball milling the graphite with liquid ammonia [13]. However, these publications did not contain either XRD data or data on elemental compositions of the new phases. It is worth mentioning results of the experiment (b) conducted by Nesting and Badding [11, 14]. They found that the amount of nitrogen incorporated into the C-N network increased with pressure, ranging from 24% (\(\text{C}_3\text{N}\)) at 18 GPa to 38% at 42 GPa (\(\text{C}_3\text{N}_{1.9}\)) [11].

As of now, the three hardest materials (diamond, cubic \(\text{BN}\ c\)-\(\text{BN}\), and \(\text{BC}_2\text{N}\)) were successfully synthesized under HPHT conditions by direct conversion of a graphite-like phase with \(sp^2\) bonding to a cubic phase with \(sp^3\) bonding [2, 3, 15, 16]. It is natural to assume that the experiment with direct conversion of the graphite-like \(\text{C}_3\text{N}_4\) to superhard phase should provide an answer to the question on the existence of the superhard \(\text{C}_3\text{N}_4\) phase. In fact, the graphitic carbon nitride was used for synthesis of new carbon nitride phases in at least three experiments. Komatsu synthesized diamond-like carbon nitride \(\text{C}_3\text{N}\) with a lattice constant of 0.351±0.001 nm (which is 1.6-1.9% smaller than that of diamond) from graphitic carbon nitride precursors (\(\text{C}_3\text{N}_2\)) by shock compression with the dynamic pressure-temperature range around 30 GPa - 3000 K [17]. Unfortunately, the sample has not been characterized by XRD: the unit cell parameter was obtained by selected area electron diffraction (SAED) attached to transmission electron microscope (TEM). In our initial attempt to transform graphite-like \(\text{C}_3\text{N}_4\) phase(s) into a diamond-like phase, we used a large-volume press and the turbostratic carbon nitride (\(t\)-\(\text{CN}\)) as the starting material. Instead of forming a dense phase, thermal decomposition of the \(t\)-\(\text{CN}\) was observed at high temperature [18].
In summary, a review of the available data on HPHT synthesis of the C$_3$N$_4$ demonstrates that although other routes such as film deposition or chemical reaction under HPHT conditions described above were not successful in synthesizing pure C$_3$N$_4$ phase, a direct transformation of the graphitic precursor into a dense phase at high pressures (>20 GPa) and high temperatures (2000K) has not been fully exploited. We present new evidence showing that phase transformation in C$_3$N$_4$ is far more complicated than we thought.

The use of the well-characterized graphitic phase [19] and the diamond anvil cell (DAC) with laser heating (LDAC) has led to the successful synthesis of a new $c$-C$_3$N$_4$ phase [4] thus providing a strong evidence that the search for the super-hard C$_3$N$_4$ is not yet finished. A cubic phase was recovered at ambient conditions from the $g$-C$_3$N$_4$ phase subjected to pressures between 21 and 38 GPa in a diamond anvil cell, laser-heated to temperatures between 1600 and 3000 K [4] (Fig. 1).

![Figure 1. Optical image of the C$_3$N$_4$ specimen after heating in DAC. Dark area of the sample is a new $c$-C$_3$N$_4$ phase heated by laser beam; the yellow part is original $g$-C$_3$N$_4$ phase, not heated by laser beam.](image)

The x-ray diffraction spectrum of the post-lasered sample recovered from 21 GPa and 1800 K is shown in Figure 2. There are 13 diffraction peaks associated with the new phase. Also seen are peaks from the diamond and from the NaCl, marked by yellow hexagons and black squares, respectively. We believed that the diamond was formed from the residual carbon material during the synthesis. The NaCl was detected in the sample [19] and we used it in this study as an independent internal pressure calibrant. Detailed analysis of the diffraction pattern of the new phase can be found elsewhere [4]. The molar volume and the density of the cubic phase are calculated as 35.126 cm$^3$/mol and 2.62 g/cm$^3$, respectively. The density of the cubic phase is less than was predicted for the high-pressure phases, but is 12% denser than the low-pressure graphitic phase ($\rho = 2.336$ g/cm$^3$). Analysis of the x-ray data on the new $c$-C$_3$N$_4$ and those of the hypothetical cubic phases, $wmII$-C$_3$N$_4$ ($a = 5.973$ Å), $dzb$-C$_3$N$_4$ ($a = 3.43$ Å) and $pc$-C$_3$N$_4$ ($a = 3.423$ Å), showed that the discrepancy of the intensities of the x-ray data between the observed $c$-C$_3$N$_4$ and the hypothetical phases ($wmII$-C$_3$N$_4$, $dzb$-C$_3$N$_4$ and $pc$-C$_3$N$_4$) could not be reconciled with the preferred orientation [4]. A unit cell with a different space group is required for explaining the intensity data on the recovered cubic phase.

The resolution of the energy-dispersive detector of an SEM was demonstrated to be sufficient for the quantitative chemical analysis of light elements such as carbon and boron [3, 20, 21]. Recovered samples of C$_3$N$_4$ in this study were measured by the JEOL JSM-5900 scanning electron microscope. Energy dispersive spectroscopy (EDS) measurements of the three samples after quenching provide C/N ratios of 1.37±0.26 which are in fairly good agreement with the EDS measurements of the C/N ratio as 1.39 in the starting material of $g$-C$_3$N$_4$ phase [19]. The new phase satisfies the rules of synthetic chemistry: (a) the elemental composition on C and N analyzed by energy-dispersive X-ray spectroscopy (EDS) indicated no loss in the nitrogen content as compared with the starting material; (b) the x-ray pattern consisting of 13 peaks could be attributed to a single phase with a cubic unit cell.
The HPHT conditions (i.e., \( P = 18 \) to 22 GPa and \( T=1600-2000 \) K) from which the \( c\)-C\(_3\)N\(_4\) phase was recovered is well within the capabilities of the large-volume press. Therefore, we have conducted synthesis of the \( c\)-C\(_3\)N\(_4\) phase in a large-volume press. The X-ray spectrum of the phase obtained in the large-volume press at pressure 25 GPa and temperature 2000 °C is similar to that shown in Figure 2. However, peaks assigned to the \( c\)-C\(_3\)N\(_4\) are weaker than those of diamonds. Only three main peaks of \( c\)-C\(_3\)N\(_4\) can be detected: peaks with \( d\)-spacing at 3.844 Å (100), 2.7347 Å (111), and 1.575 Å (211). Intensity of the prominent peak at 2.7347 Å is three times as low as intensity of (111) peak of diamond at 2.060 Å. The relative abundance of diamond and \( c\)-C\(_3\)N\(_4\) observed in the run with the large-volume press is not fully understood. We speculate that the kinetics of heating play a major role in the \( g\)-C\(_3\)N\(_4\) under HPHT conditions. A transformation of \( g\)-C\(_3\)N\(_4\) → \( c\)-C\(_3\)N\(_4\) most likely occurs in a P/T condition being far from a thermodynamic equilibrium and requiring very rapid heating. The much slower heating as performed in the large-volume press may not be as efficient as in the DAC for the formation of the \( c\)-C3N4 phase. The abundance of diamond is probably not due to the thermal decomposition reported earlier for the turbostratic carbon nitride (t-CN) [18]. This is because our sample was sealed in a Pt capsule, in contrast to the unsealed turbostratic carbon nitride (t-CN) sample used in the previous experiment [10].

Figure 2. X-ray diffraction pattern of the new phase recovered at ambient condition: (a) \( d\) spacing ranges from 4.0 to 0.9 Å. The diffraction lines from the cubic C\(_3\)N\(_4\) phase are indexed; (b) \( d\)-spacing ranges from 2.5 to 0.9 Å. The diffraction lines from the cubic C\(_3\)N\(_4\) phase are labelled as red circle (●), from NaCl as black square (■), and from diamond as yellow hexagon (◇).

Synthesis of the new \( c\)-C\(_3\)N\(_4\) phase became possible because of availability of the pure graphitic phase, \( g\)-C\(_3\)N\(_4\) produced by Guo et al. [19]. It is likely that the path of the phase transition in the C\(_3\)N\(_4\) system under HPHT conditions is dependent on the structure and purity of the starting \( g\)-C\(_3\)N\(_4\) phase and therefore comprehensive characterization of the starting \( g\)-C\(_3\)N\(_4\) phase is of importance for successful synthesis of the new superhard C\(_3\)N\(_4\) materials. Raman spectroscopy is commonly used for characterization in chemistry, because vibrational information is very specific for the chemical bonds in molecules. Raman spectroscopy has been already applied for characterization of \( g\)-C\(_3\)N\(_4\) phases [22]. Unfortunately, the strong fluorescence and photoluminescence that accompany visible Raman excitation of graphitic phases limits the sensitivity that these Raman excitation wavelengths are able to achieve [23]. We report here the use of UV Raman excitation (244 nm) and compare the spectral information content of UV and visible Raman excitation of the graphitic \( g\)-C\(_3\)N\(_4\) phase. The UV Raman spectra at 244 nm were excited using a frequency-doubled Ar ion laser (85-SHG, Lexel Laser Inc., Fremont, CA, USA). The spectra were collected on a 40× objective using Renishaw confocal Raman microscope “inVia”. Raman spectra were collected by varying the acquisition times with sample rotation. The Raman spectrum of the \( g\)-C\(_3\)N\(_4\) phase excited with UV laser at 224 nm is shown in Figure...
3. Peak fitting analysis was conducted using “Grams Software” (version 7.02, Thermo Fisher Scientific, Inc). The UV Raman spectrum of the g-C3N4 (Fig. 3) is drastically different from that measured with visible Raman spectroscopy (514 nm) [24]. A typical Raman spectrum of the g-C3N4 phase obtained with visible Raman spectroscopy has two main overlapping bands at 1357 cm$^{-1}$ (D band) and 1560 (G-band) and one or two weak bands at approximately 700 cm$^{-1}$ [24]. By analogy with graphite the Raman peaks of the g-C3N4 phase are called as D (1357 cm$^{-1}$) and G (1560) peaks [25]. The D peak does not appear in the UV Raman spectra of g-C3N4. This phenomenon was discussed in detail by Bormett et al. [23]. The most prominent feature found on the UV Raman spectra of g-C3N4 (Fig. 3a) is a sharp peak at 690 cm$^{-1}$ (28). Numbers in parenthesis are full width at half-maximum (FWHM) of the correspondent peaks. Similar mode centered approximately at 699 cm$^{-1}$ has been already detected in carbon nitride films prepared by magnetron sputtering [26]. It was suggested that the curvature of the graphene planes observed in CN$_x$ films might induce these new Raman bands. We believe that the origin of the peak at 693 cm$^{-1}$ is related to the vibration of the s-triazine rings (C$_3$N$_3$) inside g-C3N4 phase. Raman active modes of s-triazine rings in different molecules have been studied theoretically [27] and experimentally [28, 29]. Melamine (C$_3$H$_6$N$_6$, 1,3,5-triazine-2,4,6-triamine) is among the simplest molecules containing the s-triazine ring. Raman spectrum of the melamine has two main peaks: at 676 cm$^{-1}$ and at 986 cm$^{-1}$ [29]. These two peaks are assigned to different types of the ring breathing modes [29]. It is natural to assign UV Raman peaks at 690 cm$^{-1}$ and at 986 cm$^{-1}$ (50) on the spectrum of the g-C3N4 to vibrations of the same breathing modes. Peak at 1725 cm$^{-1}$ (50) is likely induced by UV radiation since it becomes weaker when sample is rotating.

![Figure 3. UV Raman (224 nm) spectra of graphitic phases: (a) g-C$_3$N$_4$ powder, integration time was 10 min, laser power was 0.4 mW; (b) g-BC$_3$ powder, integration time was 5 min, laser power was 0.2 mW.](image)

The phase transition for graphitic-like C$_3$N$_4$ to an unknown high-pressure phase, followed retrogressively by a cubic C$_3$N$_4$ at ambient conditions, is the first of its kind and is quite different from the well-known, pressure-induced transformations of graphite (or graphitic phase) to diamond (or diamond-like phase) in the C-B-N compounds. The comprehensive characterization of the novel c-C$_3$N$_4$ phase will shed light on a fundamental question regarding the nature of the bonding of the N atoms in C$_3$N$_4$ in a cubic unit cell. The finding of the new C$_3$N$_4$ phase demonstrates that the search for the new dense C$_3$N$_4$ phases is not over. Further studies of the behavior of the g-C$_3$N$_4$ phase over wide ranges of pressures and temperatures should provide an answer to the question on the existence of the superhard C$_3$N$_4$ phases.
3. Synthesis of the diamond-like BC$_3$ phase

Despite numerous efforts to synthesize a new high-pressure phase from the B-C-N triangle [30], successful synthesis of a cubic phase in the ternary B-C-N system either in a diamond-anvil cell (DAC) [2, 3] or in a large-volume press [3] was achieved only recently. Now, considerable effort has been concentrated on the synthesis of diamond in boron-rich systems [21, 31]. One of the most interesting properties found in boron-doped diamond is its behaviour at low temperature. The graphitic phase of BC$_3$ is predicted to be a superconductor with a relatively high superconducting temperature ($T_c \approx 22$ K) [32]. Superconductivity was found in boron-doped diamond synthesized at high pressure ($\approx 9$ GPa) and temperature (2,500–2,800 K) [33]. The nature of the superconductivity in boron-doped diamond is under theoretical consideration [34], and we believe that new diamond-like B-C phases should be helpful in understanding the nature of the superconductivity in the B-C systems.

Recently, Lowther examined the properties of some potential super-hard diamond-like boron–
carbon phases using \textit{ab initio} computational modelling [35]. Theoretical simulations of pressure- and temperature-induced phase transition in the B-C system demonstrated that incorporation of the B atoms into a diamond structure should not lead to the drastic distortion of the cubic cell of a diamond. The unit cells predicted by Lowther (i.e., 3.745 Å for cubic BC and 3.642 Å for nearly cubic BC$_3$) are slightly larger than that of diamond (3.5667 Å). A new superhard tetragonal ($t$-BC$_3$; $a = 3.513$ Å; $c = 3.871$ Å) phase was also predicted by Liu \textit{et al.} according to the first-principles calculations [36]. The $t$-BC$_3$ phase derived from the cubic diamond structure has been predicted and constructed by an alternately stacking sequence of metallic CBC and insulating CCC blocks along the $c$ axis, forming an ideal sandwich-like metal-insulator lattice at the atomic level with relatively high symmetry but low isotropy. Han and Ihm theoretically considered the behavior of hard materials in the presence of vacancies or impurities [37]. Calculations showed that “boron substitution results in a substantial relaxation of atomic positions and a large reduction in bulk modulus”, and that the doping of B atoms successfully produces conducting holes. The absence of lone pairs in B allows a significant amount of inward relaxation of B atoms, and these result in partial $sp^2$-type bonding between B and C. In summary, it may be concluded that first-principle calculations predict new diamond-like BC$_3$ phases with unusual electronic properties. However, substantial questions remain concerning the phase P-T-diagram of the BC$_3$ system and regularities of formation of superhard phases in this system.

A recent attempt to obtain a cubic phase in the B-C system [21] from the graphite-like BC$_3$ ($g$-
BC$_3$) was not successful as the $g$-BC$_3$ phase decomposed into B$_4$C and the boron-doped diamond with 1.8 at.%B at 20 GPa and 2300 K in a multianvil press. To avoid decomposition of the graphite-like BC$_3$ into diamond and B$_4$C, we conducted synthesis in the diamond-anvil cell (DAC) under pressure higher than 20 GPa. A direct transformation from the $g$-BC$_{1.6}$ phase to a new cubic BC$_{1.6}$ phase was obtained at high temperature, 2230 ± 140 K, and high pressure, 45 GPa [38, 39]. It was found that the x-ray diffraction spectra of the diamond-like BC$_3$ phases are very similar to those of the bulk diamond, making it difficult to distinguish a new phase from those of the diamond. The important evidence for phase identification was provided by Raman spectroscopy [39]. In this report, we present results of the Raman scattering studies on the novel $d$-BC$_3$ phase obtained under HPHT conditions.

A $g$-BC$_3$ was heated in the DAC to 2055 ± 103 K at 19 GPa (specimen denoted as $gp$-BC$_3$ as it was studied after compression), and to 2033 ± 241 K at 50 GPa (specimen denoted as $d$-BC$_3$). The BC$_3$ specimens were quenched and recovered outside the DAC. The elemental composition of the $d$-BC$_3$ phase was studied by SEM (JEOL JSM-5900 SEM) equipped with an energy-dispersive detector. The EDS measurements of the post-laser heated sample conducted at several points inside the specimen provide an average value for C/B ratio: C/B = 3.21 ± 0.14. The C/B composition was found to be homogeneous over the central area of the sample surface. The C/B ratio of the starting material B-C phase was not measured by EDS, but we assumed it was not changed in DAC during heating and compression. Raman spectra were measured by a modular Raman system (“Nanofinder 30”, Tokyo Instruments, Inc.). The Raman signal was excited by a continuous wave (with wavelength of 633 nm) He-Ne laser from Melles Griot.
Figure 4. Raman spectrum (633 nm) of BC₃ phases: (a) gp-BC₃ phase, integration time was 1.5 min, laser power was 2 mW; (b) d-BC₃ phase integration time was 4 min, laser power was 2 mW.

Raman spectra of the gp-BC₃ and d-BC₃ phases are shown in Figure 4 and the UV Raman spectrum of the graphitic g-BC₃ phase is shown in Figure 3b. The UV Raman spectrum of the graphitic g-BC₃ phase has one strong peak at 1582 (81) cm⁻¹. Its appearance is similar to Raman spectra of graphite [40] and h-BN [41], but it is substantially different from the UV Raman spectrum of the g-C₃N₄ (Fig. 3a). The spectrum of the of the gp-BC₃ phase (Fig. 4a) obtained at relatively low pressure, 19 GPa, has two broad bands D and G at 1348 (181) cm⁻¹ and 1572 (124) cm⁻¹. The appearance of the Raman spectrum of d-BC₃ phase (Fig. 4b) clearly indicates that a phase transformation (from g-BC₃ phase to d-BC₃ phase) has occurred. D and G peaks are invisible on the Raman spectrum of the d-BC₃ phase indicating that graphitic phase completely transformed into the new phase. This result is in agreement with the observation that the G band is evident at low B concentrations and at higher B concentrations, it disappears [42]. The lower spectrum is typical of many results previously obtained for B-doped diamonds [43]. It displays a broad peak at 490 cm⁻¹ (137), a second weaker peak at 1231 cm⁻¹ (97), broad peak at 671 cm⁻¹ (103), a much narrower peak around 1305 cm⁻¹ (30), and then a strongly asymmetric dip around 1340 cm⁻¹. Based on the supercell calculations, the peak observed around 500 cm⁻¹ was attributed to the Raman active stretching modes of B-B dimers [43, 44]. The peak at 1231 cm⁻¹ has been detected in B doped diamonds; its origin is uncertain, but its band position is found to agree well with the maximum in the phonon density of states of the diamond and could be connected with a relaxation of the wave vector selection rules [42]. The broad band at 1158 cm⁻¹ is probably due to sp² C species at grain boundaries [45]. It was found that at high B concentrations, this peak is hidden beneath the 1231 cm⁻¹ peak [42]. The peak at 671 cm⁻¹ has not been detected on the Raman spectra of B doped diamond; however it was mentioned that “a new feature at ~600 cm⁻¹, which is weakly present in the spectrum from the undoped sample, also increases with B content” [42]. It may be characteristic to the BCₓ phases with a high concentration of B. The spectrum of the d-BC₃ has a Fano-related dip at 1267 cm⁻¹. As it follows from the experiments, the only B-doped diamond samples “displaying the 500 and 1000 cm⁻¹ peaks, the bump around 1230 cm⁻¹ and the Fano-related dip around 1270 cm⁻¹ were found to become superconducting” [43]. It allows suggesting that d-BC₃ phase may become a superconductor at low temperatures. The small peak at 303 cm⁻¹ has not been detected in the B-doped diamond. In order to achieve a better understanding of the relationship between the Raman frequencies and the composition of the diamond-like BCₓ phases, we need to develop a comprehensive theoretical approach describing Raman active vibrational modes. Such approach should also take into account the effect of the random distribution of B and C atoms over the crystal lattice of d-BCₓ.
4. Conclusions
Two new phases ($c$-C$_3$N$_4$ and $d$-BC$_3$) have been synthesized by direct transformation from graphitic phases under HPHT conditions.

The $c$-C$_3$N$_4$ phase was recovered at ambient conditions from the $g$-C$_3$N$_4$ phase subjected to pressures between 21 and 38 GPa in a diamond anvil cell, laser-heated to temperatures between 1600 and 3000 K. The x-ray diffraction data on the new phase are best explained by a cubic unit cell with the lattice parameters $a = 3.878\pm0.001$ Å. The synthesis of the $c$-C$_3$N$_4$ phase has been also conducted in a large-volume press (at pressure 25 GPa and temperature 2000 °C). The X-ray peaks assigned to the $c$-C$_3$N$_4$ are found to be weaker than those of diamonds. The relative abundance of diamond and $c$-C$_3$N$_4$ observed in the run with the large-volume press is not fully understood. Application of the UV Raman spectroscopy for characterization of the $g$-C$_3$N$_4$ phases demonstrated that UV Raman spectra $g$-C$_3$N$_4$ phases are substantially different from that measured with visible Raman spectroscopy. It has two strong peaks at 690 cm$^{-1}$ and at 986 cm$^{-1}$ assigned to different types of the ring ($s$-triazine ring) breathing modes.

A diamond-like BC$_3$ has been synthesized at temperature 2033 K and at pressure 50 GPa. The conclusion about the phase transition from $g$-BC$_3$ to diamond-like $d$-BC$_3$ phase was drawn from Raman scattering measurements. The Raman spectrum of the novel $d$-BC$_3$ displays a broad peak at 490 cm$^{-1}$, a second weaker peak at 1231 cm$^{-1}$, another broad peak at 671 cm$^{-1}$ a much narrower peak around 1305 cm$^{-1}$, and then a strongly asymmetric dip around 1340 cm$^{-1}$. All these features except the peak at 671 cm$^{-1}$ are characteristic to the Raman spectrum of the B-doped diamond. The peak patterns of the $d$-BC$_3$ suggest that this phase could become a superconductor at low temperatures.

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