Novel binary and ternary phases in the Si–C–N system

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The present article reviews recent advances in synthesis of novel phases in the ternary Si–C–N system. A dense carbon nitride phase, C$_2$N$_2$(NH), was synthesized for the first time at high pressures and high temperatures in a laser heated diamond anvil cell (LH–DAC). Based on results of electron diffraction, EELS- and SIMS-measurements combined with theoretical calculations the structure of this new C–N–H compound was analyzed to be a defect wurtzite structure of the sinocite (Si$_2$N$_2$O)-type. Further, a variety of amorphous SiCN phases and the first ternary crystalline phases, namely Si$_3$(N$_2$C)$_2$ and Si$_7$N$_2$(NCN), were synthesized at ambient pressure. In general, the high-pressure polymorphs of Si–C–N materials are expected to exhibit a unique combination of high hardness, thermal stability and oxidation resistance with interesting optoelectronic properties.

1. Introduction

Materials with composition from the ternary Si–C–N system are of great technological importance. Diamond, the high-pressure polymorph of carbon, is the hardest material known and is widely used today for different grinding and cutting applications. Si$_3$N$_4$- and SiC- based ceramics are well known industrial materials exhibiting such technologically useful properties as high hardness, wear and oxidation resistance, chemical and thermal stability. A few hypothetical polymorphs of C$_3$N$_4$ were predicted to be competitive with diamond in hardness and stiffness. In contrast to numerous studies on binary C–N, Si–N and Si–C phases, investigations of ternary Si–C–N compounds remained sparse. In this paper we summarize the latest developments in synthesis of binary and ternary compounds within the Si–C–N system. In particular, we present the results on synthesis of a novel crystalline carbon nitride phase, C$_2$N$_2$(NH), as well as on amorphous SiCN compounds and the first ternary crystalline phases of Si(NCN)$_2$ and Si$_3$N$_2$(NCN).

In 1980 it was predicted that a few hypothetical low compressible carbon (IV) nitride polymorphs (e.g. $\beta$-C$_3$N$_4$ isostuctural to $\beta$-Si$_3$N$_4$) could have bulk moduli and hardness comparable to or even exceeding those of diamond. Since then a number of experimental efforts have been devoted to synthesize crystalline carbon nitride using different deposition and high-pressure techniques. However, the obtained C–N phases were predominantly amorphous or nanocrystalline with structure and composition being not unambiguously determined. Therefore, the existence of pure crystalline C$_3$N$_4$ polymorphs remains a matter of controversy within the scientific community. Nevertheless, as a direct consequence, the search for novel super-hard materials with additional useful properties has attracted much attention during the last years. In addition to the C–N system, there are other binary, ternary and quaternary compounds of light elements in competition. They are, for example, Si–N, Si–C–N, B–C–N, Al–C–N, Si–B–C–N, etc. These non-oxide materials are expected to possess a favorable combination of hardness, oxidation resistance and chemical inertness.

As a result of this research, in 1999 a novel cubic phase of silicon nitride ($\gamma$-Si$_3$N$_4$) having spinnel structure was synthesized at high pressures and high temperatures using a LH–DAC. This material was found to have high elastic moduli and very high hardness (about 40 GPa) as well as to possess exceptional thermal stability, when compared to traditional $\alpha$- and $\beta$-Si$_3$N$_4$. Surprisingly, no experimental attempts to investigate the formation of intermediate compounds in the Si$_3$N$_4$–C$_3$N$_4$ system at high pressures and high temperatures were reported so far.

2. Synthesis of carbon nitride imide, C$_2$N$_2$(NH)

As mentioned in the introduction, research on carbon nitrides was initiated by theoretical predictions that saturated (sp$^3$-hybridised) carbon (IV) nitride phases, in particular $\beta$-C$_3$N$_4$, can be as hard as or even harder than diamond. The results of enormous amounts of theoretical and experimental studies on carbon nitrides, performed during the last two decades, are summarized and critically analyzed in several review articles. The experimental attempts to synthesize crystalline carbon nitride have exploited various techniques such as chemical (CVD) and physical (PVD) vapour deposition, static (multi-anvil, DAC) and dynamic (shock-waves) high-pressure methods. Furthermore, various single-source carbon-nitrides (e.g. C$_3$N$_3$(NH)$_2$), C$_2$N$_2$, C$_3$N$_4$, C$_3$N$(\text{Cl})_3$ or mixtures of carbon (graphite, C$_60$, C$_{60}$) and monomer or polymer precursors.
with nitrogen sources (e.g. N₂, NH₃, Li₃N, NH₂NH₂) were employed as starting materials. However, the obtained C–N materials were predominantly amorphous or nanocrystalline with low nitrogen content and structures being not unambiguously determined. Furthermore, compounds prepared at high-pressures were not generally recovered to ambient conditions.

In 2007 we reported on the high-pressure high-temperature synthesis of a well-crystallized carbon nitride imide, C₂N₂(NH), in a LH–DAC from a single source precursor, namely dicyandiamide, C₂N₄H₄ (Scheme 1). The starting material was embedded in a NaCl pressure medium within a hole in the preindented stainless steel gasket, squeezed to required pressure and heated with radiation of a CO₂-laser. After synthesis the products were examined in-situ by Raman spectroscopy. The recovered samples were washed by dissolving NaCl in distilled water and examined using transmission electron microscope (TEM) equipped with an electron energy-loss spectrometer (EELS) and EDX-detector.

Scheme 1. Reaction scheme for synthesis route of C₂N₂(NH). P and T is pressure and temperature, respectively.

Treatments of dicyandiamide at P < 27 GPa and T < 1700°C yielded black amorphous products. At higher P–T conditions the formation of a new optically transparent phase having characteristic Raman spectrum was observed. Transmission electron micrograph investigation of the recovered products revealed the presence of well crystalline material (Fig. 1a, b). The size of crystallites was found to increase with pressure and heating duration. Prolonged heating (about 20 min) at temperatures > 1700°C and pressure of 41 GPa resulted in the formation of crystallites up to 1.5 µm in size (Fig. 1a). The C:N ratio in the crystals was determined from the EELS spectra to be 0.62 ± 0.06. No oxygen was detected by EELS, indicating its concentration below 0.1–1 at. %. Nano-SIMS measurements revealed the presence of hydrogen in the recovered crystals with H:C ratio of 0.5 ± 0.15. Thus, the resulting composition of synthesized material can be expressed by formula C₃N₄H. The energy-loss near-edge structure (ELNES) of EELS spectra was used to obtain information on the local coordination environments of the atoms. Pre-edge features at the C–K and N–K edges (Fig. 2) are identified as transitions to σ* molecular orbitals, thus indicating tetrahedrally-directed sp³ hybridized orbitals for both C and N atoms in the synthesized material.

The crystal structure of the new compound was determined by a combination of selected area electron diffraction (SAED) data, experimentally measured composition and first-principles theoretical studies. The structures suggested for hypothetical CN₄ were subsequently excluded due to high internal energy, inherent elastic and dynamic instabilities, or by their incompatibility with the observed lattice parameters and the SAED intensities. Only a defect-wurtzite structure type gave good agreement with the electron diffraction and EELS data, especially regarding the σ* core-loss edges (K edges) are identified as transitions to σ* molecular orbitals, thus indicating tetrahedrally-directed sp³ hybridized N sites. The analysis of SAED patterns from different zones resulted in an orthorhombic C-centered cell with a = 0.7546(9) nm, b = 0.4434(8) nm and c = 0.4029(8) nm. The cell parameters obtained from first principle calculations, a = 0.75726 nm, b = 0.44425 nm and c = 0.40036 nm, are in good agreement with the experimentally determined ones. This finding supports the defect-wurtzite structure type for C₃N₄(NH). With space group Cmc₂, the structure of the new compound (Fig. 3) was found to be analogous to those of Si₃N₄(NH) and Si₃N₄O (sinoite). In some cases, sinoite occurs with meteorites. Moreover, an excellent agreement was found between experimentally mea-

![Fig. 1. TEM investigations: (a) A crystal of the C₂N₂(NH) sample synthesized at P = 41 GPa and T > 1700°C, bright field TEM. (b) Selected area electron diffraction (SAED) pattern of zone [001]. The pseudo-hexagonal appearance reflects the relation to the wurtzite-type structure.](image1)

![Fig. 2. EELS investigation: representative C-K and N-K core-loss edges of C₂N₂(NH) where the grey shaded areas indicate the 60 eV wide integration windows started from the edge onsets. Transitions to σ* molecular orbitals are labelled. The EELS spectra of C-K and N-K edges calculated for C₂N₂(NH) using full multiple scattering (FMS) theory are shown below.](image2)

![Fig. 3. Crystal structure of the defect wurtzite (sinoite-) type carbon nitride imide, C₃N₄(NH). Space group Cmc₂, (No. 36), a = 0.7555 nm, b₀ = 0.4453 nm, c₀ = 0.403 nm.](image3)
sured EELS spectrum and ELNES at the C–K and N–K edges of C$_2$N$_2$(NH) (Fig. 2) calculated using self-consistent full multiple scattering (FMS) theory. The theoretical density of carbon nitride imide (3.21 g/cm$^3$) and its atomic density (172.7 atoms/nm$^3$) are close to those of diamond (3.52 g/cm$^3$ and 176.5 atoms/nm$^3$, respectively). The bulk modulus of C$_2$N$_2$(NH) has been calculated to be 277 GPa, which is significantly lower than those for diamond or the predicted dense C$_2$N$_2$ polymorphs ($B_0 = 430–460$ GPa), but is unusually high for a carbon nitride compound containing stoichiometric amount of hydrogen.

Dicyandiamide, C$_4$N$_4$H$_4$, was chosen as a starting material for high-pressure synthesis of carbon nitride compounds because of its alternating C–N units and N:C ratio > 4:3. It was supposed that condensation into C$_3$N$_4$ would occur by elimination of 4/3 equivalents of NH$_3$. However, under our reaction conditions, only 1 equivalent of NH$_3$ was eliminated to give C$_2$N$_2$(NH) (Scheme 2a). Assuming a further similarity of C$_2$N$_2$(NH) to Si$_2$N$_2$(NH), one may propose a formation of dense C$_2$N$_2$ polymorphs under more extreme $P$–$T$ conditions analogous to the Si$_2$N$_4$ synthesis route. According to this route, α-Si$_2$N$_4$ is synthesized via high-temperature ammonolysis of SiCl$_4$ through the intermediate silicon nitride imide, Si$_3$N$_2$(NH) (Scheme 2b).$^{41,42}$ Thus, the new carbon nitride imide can be considered as an intermediate compound on a path leading to formation of dense C$_3$N$_4$ phases.

![Scheme 2. Reaction schemes of the proposed synthesis route for C$_3$N$_4$ (a) and of synthesis route for Si$_3$N$_4$ (b) (see text).](image)

It should be also mentioned that in contrast to non-cyclic dicyandiamide (C$_4$N$_4$H$_4$), the use of cyclic compounds such as melem (C$_6$N$_{10}$H$_6$) and melon ([C$_6$N$_{9}$H$_3$]$^-$) as starting materials for high-pressure high temperature synthesis resulted in amorphous CN$_x$ products with low nitrogen contents ($x = 0–0.5$), exclusively.$^{43}$ Moreover, despite the favourable $P$–$T$ conditions, the formation of diamond has never been observed. This fact is in agreement with earlier experimental observations,$^{44}$ where the presence of nitrogen in precursors did not favour the formation of diamond.

### 3. Synthesis of ternary SiC$_N$ phases

Silicon nitride and silicon carbide are totally immiscible: the solubility of C in Si$_3$N$_4$ is below 1%. Therefore, in order to synthesize ternary Si–C–N compounds different non-equilibrium routes are usually employed, such as CVD, PVD and pyrolysis of polyorganosilazanes (POPOS). In the last method thermally induced ceramisation of poly-(hydridomethyl)-silazane results in the formation of amorphous Si–C–N compounds with nitrogen- and silicon-rich compositions (e.g. Si$_3$C$_2$H$_{11}$N$_5$, Si$_3$C$_2$N$_{16}$ and Si$_3$C$_2$N$_{14}$, see Fig. 4).$^{45,46}$ These amorphous silicon carbonitrides are stable up to 1450°C and crystallise into Si$_3$N$_4$/SiC composites at higher temperatures. Crystalline ternary Si–C–N phases obtained by CVD and PVD methods typically possess a modified α-Si$_3$N$_4$ structure.$^{49,50}$ Carbon incorporation into this structure is again very limited and does not exceed 6 at. %. In 1997 the first crystalline carbon rich Si–C–N compounds, Si$_2$C$_2$N$_4$ and Si$_3$C$_2$N$_4$, situated on the hypothetical C$_3$N$_4$–Si$_3$N$_4$ tie line of the ternary Si–C–N phase diagram (Fig. 4), were synthesized.$^{51,52}$ Both compounds were found to contain the carbodiimide ‘‘–N=C=N–’’ unit (NCN): SiC$_2$N$_4$ and Si$_3$C$_2$N$_4$. Crystalline silicon dicarbodiimide, Si(NCN)$_2$, was synthesized by thermal treatment of the amorphous polymer [Si(N=C=N)$_2$], at 400°C. At 150°C the obtained high-temperature Si(NCN)$_2$ phase undergoes a reversible phase transition. The X-ray powder diffractionogram of the room temperature phase displays very broad peaks, which can be attributed to the small particle size of 10–20 nm. The presence of carbodiimide units at T $>$ 150°C is proven by $^{13}$C MAS–NMR and FT–IR spectroscopy.

From X-ray powder diffraction data the high-temperature Si(NCN)$_2$ phase was found to have a cubic structure, space group $Pn$3$m$ (No. 224) (Fig. 5a). The structure type can be considered as anti-cuprite (Cu$_2$O) where Si occupies the O-site and the N=C=N group replaces the Cu-atoms. The structure is closely related to the structure of the SiO$_2$–phase β (high) cristobalite since the anti-cuprite structure can be considered as two interpenetrating β-cristobalite-networks. This relationship illustrates the pseudo-chalcopyritic character of the ternary [N=C=N]$^{2–}$- anion which has a group electronegativity comparable to that of the O$^{2–}$ anion.$^{56}$ Silicon dicarbodiimide was found to be thermally stable up to 900°C in argon atmosphere.

At higher temperatures Si(NCN)$_2$ decomposes with mass fraction loss of about 0.4 via elimination of C$_2$N$_2$ and N$_2$, as analyzed by mass spectrometry/thermal gravimetric analysis (MS–TGA). The final product was found to have elemental composition of Si$_2$C$_n$ as well as to contain carbodiimide units. The crystals of this material, silicon-(carbodiimide)-nitride, Si$_3$N$_4$(NCN), have a
ters comprised of alternating C–N or Si–N units perpendicular to feature of these sinoite-related structures is the existence of layer structure. In Fig. 6b the lack of a horizontal mirror plane is evident. The bulky NCN-group in Si2N2(NCN), however, links the layers crosswise which contributes to stiffen the architecture of the new setting of space group No. 41 becomes $B ba_2$. The common feature of these sinoite-related structures is the existence of layers comprised of alternating C–N or Si–N units perpendicular to the longest axis. These layers are connected by $O^2-$atoms, $[NH]^-$ or $[NCN]^2-$groups, respectively. In the case of sinoite and $C_3N_2(NH)$ the connecting atoms are placed on mirror planes. The bulky NCN-group in $Si_3N_4(NCN)$, however, links the layers crosswise which contributes to stiffen the architecture of the structure. In Fig. 6b the lack of a horizontal mirror plane is observable.

Above 1200°C silicon-(carbbodiimide)-nitride decomposes into $Si_3N_4$, C and N2.

With respect to experimental high-pressure research on Si–C–N compounds, only room temperature (RT) compressibility study for crystalline $Si_3N_4(NCN)$ was reported.59 The authors indicated that no transformation of $Si_3CN_4$ to other crystalline or amorphous phase was observed up to 8 GPa at RT. Very recently we performed RT high-pressure studies of $Si_3N_4(NCN)$ up to 20 GPa in a diamond anvil cell using angle-dispersive X-ray powder diffraction combined with synchrotron radiation (beam-line ID27, ESRF, Grenoble, France). In agreement with earlier studies, the diffraction peaks of $Si_3N_4(NCN)$ broaden and weaken considerably with pressure increase. At pressures above 10 GPa the diffraction peaks have almost disappeared, thus indicating complete amorphisation of initially nanocrystalline $Si_3N_4(NCN)$. The samples recovered to ambient conditions were found to maintain the amorphous state. The future work on Si–C–N system should be focused on evaluation of possible reaction conditions (temperature and N2 pressure) which could allow Si(NCN)2 and/or Si2N2(NCN) either to partition into $C_3N_4$ and $Si_3N_4$ or to form novel dense high-pressure polymorphs.

4. TEM studies of amorphous SiCN phases

High-resolution transmission electron microscopy (HR-TEM) is a very helpful tool for characterization of the phase content of multi-component micro- and nanostructures. It also allows the unequivocal identification of amorphous phases in contrast to crystalline ones. Nanosized regions can be characterized due the high lateral resolution (and small beam diameter) applicable during TEM imaging. In addition to conventional TEM characterization (imaging and electron diffraction), local chemical analysis of the corresponding phases can be performed using, for example, electron energy-loss spectroscopy (EELS) or energy-dispersive X-ray analysis (EDX). In particular, TEM combined with EELS was used for structure determination of novel carbon nitride phase (s. Chapter 1 of this review, Figs. 1, 2) as well as for identification of the nanocrystalline SiCN phase (s. Chapter 2, Fig. 6).

Conventional and high-resolution TEM imaging was employed to study the micro/nanostructure evolution of polymer-derived SiCN ceramics, depending on annealing temperature, starting precursor composition and precursor architecture. In the SiCN system, crystallization into the thermodynamically stable phases occurs at higher temperatures, as for example compared to the ternary SiCO compound. Initially, all polysilazane-derived SiCN materials pyrolyzed at temperatures between 800–1000°C reveal an amorphous microstructure, as shown in Fig. 7. It should be noted that PDCs typically, independent of composition, reveal an amorphous microstructure upon pyrolysis. The high-resolution TEM image to the right is a Fourier-filtered image of the amorphous matrix, which allows the reduction of electron diffraction pattern is also shown as inset.

Fig. 5. Crystal structures: (a) cubic $Si(NCN)_2$, space group $Pn 3m$ (No. 224), lattice parameter $a_0 = 0.619$ nm; figured is the content of a box of thickness $a_0$ and of $2a_0$ height and width. One of the two cristobalite-type networks is distinguished by pale contrast. (b) orthorhombic $Si_2N_2(NCN)$, space group $A ba_2$ (No. 41), lattice parameters $a_0 = 0.544$ nm, $b_0 = 1.358$ nm, $c_0 = 0.481$ nm. Cf. Fig. 6b.

Fig. 6. a) TEM: Nanocrystalline $Si_2N_2(NCN)$ obtained at 960°C from $Si(NCN)_2$. b) HRTEM, zone [001], contrast inverted for clarity, structure superimposed. The lack of a horizontal mirror plane is evident.

Fig. 7. HRTEM: High-resolution TEM image (left) of a typical amorphous SiCN material upon annealing at 1000°C. The composition was analysed to be $SiC_{11}N_{83}$. The Fourier-filtered image (right) reveals a higher magnification of the boxed area shown in (a). The corresponding electron diffraction pattern is also shown as inset.
background noise of the original HRTEM image (left). Worm-like microstructural features are clearly visible, characteristic for the amorphous nature of the material. The inset shows a selected area electron diffraction pattern (SAD) of the SiCN material. The elastically scattered diffuse halo of the SiCN matrix is typical of the amorphous SiCN network. These studies underlined that the architecture of the starting polymer affects the network structure of the glass formed after the thermal organic-inorganic transition.

Annealing at higher temperatures typically introduces local crystallization of the thermodynamically stable phases, as illustrated by the formation of turbostratic graphite in Fig. 8. The Fourier-filtered image (right) reveals a magnification of the boxed area indicated in (a). Clearly, the onset of ordering of excess carbon in this system was observed upon thermal anneal at 1400°C. In addition, the corresponding electron diffraction pattern (inset) shows a clear difference to the SAD pattern recorded upon pyrolysis at 1000°C, which is due to the formation of both turbostratic carbon and nanosized SiC precipitates. Hence, annealing at higher temperatures triggers the redistribution of excess free carbon in this system and leads to the formation of the thermodynamically stable SiC phase. It should be noted that, depending on starting composition, the crystallization of the corresponding high-temperature phases can be quite different; e.g., the formation of SiN4 as opposed to the precipitation of predominantly graphite and SiC.

5. Computational studies in the Si–C–N system

In contrast to a numerous theoretical studies on carbonitrides, investigations of ternary compounds within Si–C–N system using computational method remained rather sparse. Since the hypothetical superhard C3N4 was initially proposed to be isostructural to β-Si3N4,36 early computational studies were generally concentrated on β-Si3N4 and β-Si2N3 modifications related to the structure of β-Si3N4.37–39 Betranhandy et al.40 have studied the properties of (Si,C)3N4 compounds employing pseudocubic structure, which was alternatively suggested for hypothetical superhard C3N4.41 The discovery of cubic spinel γ-Si3N4 in 199942 motivated theoretical studies on spinel-type Si–C–N compounds. Ching et al.43,44 suggested that only γ-Si3C2N4 is stable with respect to decomposition to γ-Si3N4 and γ-C3N4. These works have shown that bulk moduli for all considered dense structures increase with increase of carbon content and reach the maximum value for binary C3N4 compound. All calculated bulk moduli values for dense Si3CN4 and SiC3N4 range from 270 GPa to 345 GPa, which suggested high hardness for these hypothetical structures. Other studies, however, have shown that for intermediate compounds, SiC3N4 and SiC3N4, the α-type structure related to α-Si3N4 (instead of β-Si3N4, or pseudocubic-C3N4 type) is the most energetically favourable.45,46 The α-type Si–C–N compounds were calculated to have the same tendency of bulk modulus to increase with carbon content and to be wide band gap semiconductors (Eg≈4 eV). Furthermore, Kroll47 pointed out that on increasing of the carbon content in (Si,C)3N4 to Si3C4 (and further to Si2C3N3) the willemite–II structure, originally proposed for superhard C3N4,48 can become accessible at pressures above 34 GPa. One should notice that none of the predicted dense crystalline ternary Si–C–N compounds of mentioned stoichiometry have been synthesized so far.

The discovery of low density crystalline Si(NCN)2 and Si2N3(NCN) phases motivated subsequent theoretical studies of their structural and electronic properties, as well as their stability with respect to decomposition and/or transformation to hypothetical dense modifications.49–53 The authors have indicated that properties of these compounds are mainly dictated by presence of carbodiimide unit, –N=C=N–, which appeared to be both highly compressible and very reactive under externally applied load. In particular, Lowther et al.49 pointed out the role of carbodiimide unit reactivity for potential high-pressure synthesis of dense Si–C–N polymorphs and suggested the transformation from Si(NCN)2 to β-Si2N3C4 to occur at pressures of 6–12 GPa. However, systematic theoretical investigation of the high-pressure behaviour of Si(NCN)2 and Si2N3(NCN) has not been yet reported.

The increase of reactivity of carbodiimide unit on compression was first theoretically studied in respect to alternative syntheses routes of C3N4 from carbodiimide precursors.50 It turned out that –N=C=N– unit will break at high pressures and react with surrounding atoms forming more saturated framework. Analogous to earlier reported procedure,51 theoretical compression experiment was performed on the structure of the low temperature orthorhombic Si(NCN)2 phase with proposed space group P42/m (No. 95). At high pressures –N=C=N– units were found to bend significantly and to break within the range of 10–20 GPa, thus resulting in formation of a denser modification of Si(NCN)2. In contrast to SiN4 environments in ambient-pressure compounds, all silicon atoms of the suggested high-pressure phase are octahedrally coordinated by nitrogen (Fig. 9). The calculated bulk modulus for high-pressure SiC3N4 (84 GPa) is significantly higher than that for ambient-pressure Si(NCN)2 (19 GPa). Similarly, first-principles calculations were performed for orthorhombic Si3N4(NCN) (space group Aba2). Upon cold compression up to 23–30 GPa, silicon-(carbodiimide)-nitride with tetrahedrally coordinated Si-atoms is likely to transform to denser orthorhombic structure with Pc-type space group. This transformation is accompanied by change of coordination geometry: one fourth of Si-atom adopt 6-fold coordination. The bulk moduli for ambient and high-pressure Si3C4N4 phases are calculated to be 110 GPa and 133 GPa, respectively.

Another important result of the ab initio molecular dynamic simulations is a strong isotropic negative thermal expansion of silicon dicarbodiimide. The calculations predict for Si(NCN)2 the thermal expansion coefficient of $-1 \times 10^{-3}$ 1°C in the temperature range between 25 and 425°C. Our subsequent experimental studies employing synchrotron radiation (at the beam-line B2, HASYLAB/DESY, Hamburg, Germany) showed that the thermal expansion of Si(NCN)2 is negative in the temperature range from...
200 to 500°C. Low crystallinity of the investigated material resulted in comparably large errors in determination of the lattice parameter. Therefore, further experiments with better quality crystals are currently under way. The predicted negative thermal expansion is attributed to the combination of tetrahedral environment of Si atoms and flexible –N=C=N– units present in Si(NCN)2, thus, is likely to be a general phenomenon of all such carbodiimide compounds.

6. Conclusion and outlook
A number of novel binary and ternary compounds within the Si–C–N system were predicted and theoretically studied during the last two decades. The first-principles calculations suggested unique combination of interesting mechanical, thermal and optoelectronic properties for proposed C–N, Si–N and Si–C–N materials. Although the existence of the most hypothetical compounds from Si–C–N system has not been experimentally confirmed so far, such predictions motivated an intensive experimental research in this field. As a result, a variety of novel compounds were discovered, such as amorphous or nanocrystalline carbonitrides CNx (0 < x < 1.33), cubic spinel γ-Si3N4, amorphous Si–C–N materials and low carbon content crystalline α-(Si,C)3N4 films. These materials were found to exhibit such technologically important properties as high hardness and fracture toughness, thermal stability, chemical inertness and, in most cases, to be wide band gap semiconductors. In this paper we have mainly concentrated on the recently discovered dense carbon nitride imide, C3N4(NH), as well as on the first crystalline ternary compounds, Si(NCN)2 and Si2N2(NCN).

The defect wurtzite-type carbon nitride imide, C3N4(NH), is the first example of well crystalline dense carbon-nitride-related phase with N:C ratio of 1.5. Its crystallographic and atomic densities were found to be close to those of diamond. The calculated bulk modulus of carbon nitride imide is even higher than those of α- or β-Si3N4. Moreover, C3N4(NH) can be considered as a starting material for high-pressure high-temperature synthesis of dense C3N4 phases via elimination of one mole of NH3. The properties of the ternary crystalline compounds Si(NCN)2 and Si2N2(NCN) are mainly determined by the presence of unique structural features, such as –N≡C≡N– units interconnecting Si atoms within the solid state structure. Being very flexible and reactive, these units account for a strong negative thermal expansion of silicon carbodiimides, as well as for high-pressure structural transformations predicted for these materials. Since the stoichiometric Si3C2N6 and SiC3N4 compounds can be considered as solid solutions between silicon- and carbon nitrides (Si3N4 + 2C2N2 = 3SiC2N4 and 2Si3N4 + C3N4 = 3Si3C2N4), the question arises whether these solid solutions can be synthesized in form of one of the suggested dense structures (e.g. α-, β- or γ-Si3N4 type, etc.). In view of the recent advances in synthesis of novel high-pressure nitrides,6,10,39,73 we believe that high-pressure high-temperature methods have a great potential for exploration of new dense binary and ternary solids in the Si–C–N system.

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