

# High-Pressure Syntheses of Novel Binary Nitrogen Compounds of Main Group Elements\*\*

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*In memoriam Holger Behrends (1975–2000)*

The application of high-pressure methods in the search for novel materials usually requires additional effort compared to syntheses at ambient pressure. Depending on the desired  $p/T$  conditions different methods may be used. Special techniques and experimental apparatus such as shock waves, diamond anvil cells, and multianvil presses, which have been applied mainly by earth scientists and physicists in the past, are increasingly being applied by synthetic chemists and material scientists. A series of fascinating discoveries have been made recently as is demonstrated by three examples of binary nitrogen compounds: 1) Diazenides, compounds with  $N_2^{2-}$  ions, were obtained as single-phase products and structurally characterized for the first time. 2) At 11 GPa and 1800 K a phosphorus(v) nitride was prepared, which contains tetragonal  $PN_5$  pyramids as a novel structural motif. 3) Macroscopic amounts of spinel silicon nitride were synthesized by shock-wave techniques, which allows the comprehensive characterization and possibly the implementation of this new hard material.

## 1. Introduction

Temperature, reaction time, and concentration or reactant ratios are without question the most widely used parameters in preparative chemistry. Another very crucial parameter for the successful performance and optimization of chemical reactions is the pressure, which is less frequently used. The major reason for this is certainly the additional experimental effort required for applying high-pressure methods.<sup>[1]</sup> The “standard high-pressure technique” in the field of synthetic chemistry is based on the application of autoclaves and high-pressure bombs. In recent years the application of these techniques was further expanded, for example for reactions in supercritical media.<sup>[2]</sup> Methods for the generation of extremely high pressures ( $p > 1$  GPa) have been developed in the fields of earth sciences. Currently, these techniques are increasingly used in preparative inorganic chemistry and material science, which is reflected by several recently published review articles.<sup>[3]</sup>

Table 1 shows a comparison of the presently most frequently used high-pressure techniques. Each of these methods represents a compromise with respect to maximum pressure, temperature, sample size, costs, and experimental effort. Autoclaves and high-pressure bombs are easy to operate, cheap, and allow the production of large samples; however, the  $p/T$  range is rather limited. “Large” presses such as belt or multianvil equipment (Figure 1) are much more expensive and more difficult to operate;<sup>[1c,d]</sup> however, they allow pressures and temperatures up to 25 GPa and 3000 K, respectively, and produce amounts of sample that permits convenient characterization with the common analytical techniques. Even higher pressures and temperatures are achievable with laser-heated diamond anvil cells (Figure 2).<sup>[1e,f]</sup> Owing to the transparency of the diamond anvils they offer the opportunity of in situ examinations, for example by vibrational spectroscopy or X-ray diffraction. Disadvantages are the small sample sizes ( $\ll 1$  mg). Consequently, energy-dispersive X-ray analysis (EDX) and electron energy loss spectroscopy (EELS) measurements in transmission electron microscopes are usually necessary to estimate the elemental composition of the products.

Shock-wave syntheses methods<sup>[1g,h]</sup> can be subdivided in three classes: 1) “flyer-plate” or “impact” methods, in which a projectile (flyer) is shot onto an especially prepared (mixture)

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Table 1. Overview of high-pressure techniques and apparatus currently used in preparative chemistry.

	Autoclaves/Pressure bombs	"Piston–cylinder-presses"	"Large" presses <sup>[a]</sup>	Shock syntheses <sup>[b]</sup>	Diamond anvil cells
$p_{\max}$ [GPa]	1.5	5	25 (40 <sup>[c]</sup> )	150 <sup>[d]</sup>	500
$T_{\max}$ [K]	1200 (2000 <sup>[e]</sup> )	2000	3000	5000	7000
sample size	1 kg (10 g) <sup>[f]</sup>	< 10 g <sup>[f,g]</sup>	0.001–1 g <sup>[g]</sup>	0.1–500 g <sup>[h]</sup>	≪ 1 mg
prime costs [€]	500–25 000	2500–75 000	50 000–400 000	> 25 000 <sup>[i]</sup>	75 000–150 000 <sup>[i]</sup>
cost of operation	low	low–moderate	high	moderate–very high	low–moderate

[a] For example, multianvil presses. [b] For example, flyer plate or detonative syntheses. [c] Using diamond-based materials for the anvils. [d] By "impact" experiments much higher pressures may be generated, but usually it is very difficult to recover the sample. [e] Using IHPV ("internally heated pressure vessels"). [f] Depending on the pressure range different types of devices are used. [g] Sample sizes strongly depend on the desired pressure range. [h] For very large samples (> 10 g), costs increase disproportionately, so that it is better to perform several experiments one after the other. [i] Strongly dependent on sample size and applied technique. [j] Including CO<sub>2</sub> or YAG laser for heating as well as equipment for in situ temperature and in situ pressure determination (Rubin-fluorescens).

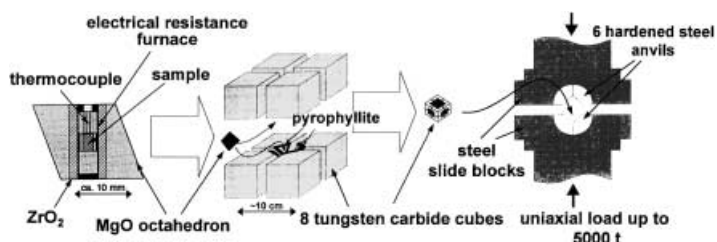


Figure 1. Schematic sketch of a diamond anvil cell.

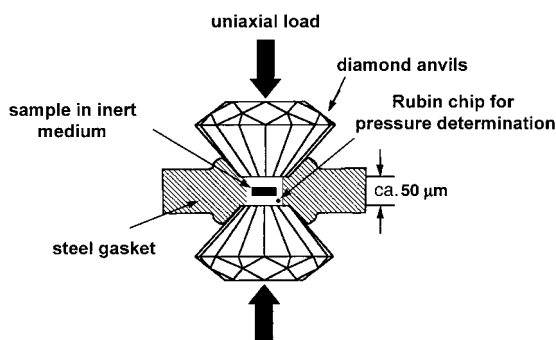


Figure 2. Schematic sketch of a two-stage cubic octahedral multianvil press.

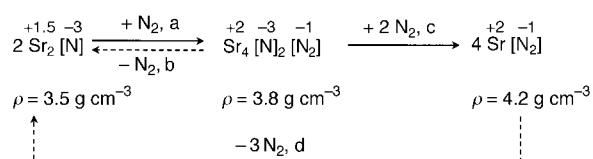
of starting materials, 2) shock compressions or compactions, which usually are based on an explosive charge, which is in direct contact with the starting materials to be densified, producing a pressure wave, and 3) detonative syntheses, in which a precursor–explosive–mixture is ignited in a suitable vessel. All three techniques offer the opportunity to produce larger amounts of products. The disadvantages of shock-wave methods are obvious: The desired  $p/T$  condition can only be perpetuated for a short time (ca. 1  $\mu$ s). Other frequently applied equipment, such as Bridgman or belt presses, was often modified and adapted to special requirements. Furthermore, there are other rarely used approaches such as the volume decrease upon solidification of melts. For all static high-pressure techniques the maximum pressure decreases with increasing temperature (strength decline) and increases with smaller sample sizes.

Similar to the field of oxides more and more research over the last few years has been concerned with ternary, quaternary and multinary nitrogen compounds.<sup>[4]</sup> That the application of high pressure provides access to new interesting binary phases today is evidenced in the following by examples of novel nitrogen compounds of the main group elements.

## 2. High-Pressure Synthesis and Structural Characterization of Diazenides

Ionic oxygen compounds such as oxides (O<sup>2-</sup>), ozonides (O<sub>3</sub><sup>-</sup>), peroxides (O<sub>2</sub><sup>2-</sup>), and hyper- or superoxides (O<sub>2</sub><sup>-</sup>) are well known;<sup>[5]</sup> a comparison with nitride compounds raises the question, whether there are, in addition to nitride and azide ions, other anionic species—for example "pernitride" ions (N<sub>2</sub><sup>2-</sup>)—that are stable in the condensed phase. There are numerous metal complexes known, in which the N<sub>2</sub> ligands may be considered as N<sub>2</sub><sup>2-</sup> or N<sub>2</sub><sup>4-</sup> ions.<sup>[6]</sup> This is particularly true for complexes of the early transition metals, which contain  $\mu$ - $\eta^1$ : $\eta^1$ -bridging N<sub>2</sub> molecules. Furthermore, N<sub>2</sub><sup>2-</sup> ions generated by ion implantation in CdS were detected by ESR spectroscopy.<sup>[7]</sup> The high-pressure synthesis of BaN<sub>2</sub> was reported in 1953.<sup>[8]</sup> Saltlike pernitrides of the alkaline earth metals containing the N<sub>2</sub><sup>4-</sup> ion have also been mentioned in literature.<sup>[9]</sup> The existence of these compounds was supported by elemental analyses, IR spectra, as well as by the detection of hydrazine in the hydrolysis products.<sup>[9]</sup> However, a structure determination of a compound with N<sub>2</sub><sup>x-</sup> ions has not been accomplished yet.

Moreover, the number of binary nitrogen compounds of alkali metals and alkaline earth metals is still relatively small.<sup>[10]</sup> For the Sr/N system, Sr<sub>3</sub>N<sub>2</sub>, Sr<sub>3</sub>N<sub>5</sub>, and SrN have been reported,<sup>[10a]</sup> but only the subnitride Sr<sub>2</sub>N<sup>[10b,c]</sup> and the azide Sr(N<sub>3</sub>)<sub>2</sub><sup>[10d]</sup> have been structurally characterized. Against this background, the high-pressure synthesis and structural characterization of "diazenides" SrN and SrN<sub>2</sub>, that is compounds with N<sub>2</sub><sup>2-</sup> ions, by Kniep et al.<sup>[11]</sup> is particularly remarkable (Scheme 1). Phase-pure SrN was synthesized starting from Sr<sub>2</sub>N at 920 K, 0.04 GPa, and a reaction time of 72 h. Increasing the pressure to 0.55 GPa under otherwise similar conditions furnished SrN<sub>2</sub>. The synthesis was carried out in a special autoclave, in which the initial N<sub>2</sub> pressure was 0.02 and 0.275 GPa, respectively.



Scheme 1. Synthesis and decomposition of the strontium diazenides SrN and SrN<sub>2</sub>: a) 920 K, 0.04 GPa, 3 d; b) 573–673 K, 100 kPa; c) 920 K, 0.55 GPa, 3 d; d) 618–673 K, 100 kPa.

The structures of SrN and SrN<sub>2</sub>, which are metastable at 20 °C and 100 kPa, were determined by X-ray and neutron diffraction using powders. SrN<sub>2</sub> crystallizes isotypically to the corresponding alkaline earth acetylides in a tetragonal distorted NaCl structure (Figure 3, left). SrN is described as a nitride-diazenide: (Sr<sup>2+</sup>)<sub>4</sub>[N<sup>3-</sup>]<sub>2</sub>[N<sub>2</sub><sup>2-</sup>]. The structure can be derived from Sr<sub>2</sub>N (inverse CdCl<sub>2</sub> type) by adding N<sub>2</sub><sup>2-</sup> ions into the octahedral sites between the Sr<sub>2</sub>N layers. The N–N distance within the diazenide ions (ca. 122.5 pm) corresponds well with that in  $\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2$  complexes, which may be considered to contain M-(N<sub>2</sub><sup>2-</sup>)-M units.<sup>[6]</sup> The N–N distances in organic *cis*- (124.5 pm) and *trans*-dialkyl diazo compounds (122.2 pm) as well as the O–O distance in the oxygen molecule (120.7 pm) are also in the same region.<sup>[12]</sup> Ab initio calculations for singlet-N<sub>2</sub><sup>2-</sup> ions gave a value of 123.8 pm, which is also very close to the results found for the solid-state structures.<sup>[13]</sup>

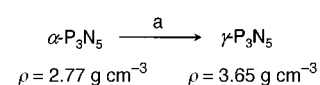
Simon and Kniep et al. have also reported the synthesis of barium pernitride, BaN<sub>2</sub>,<sup>[14]</sup> which was obtained from the elements at 0.56 GPa and 920 K or by careful thermal decomposition of dry barium azide Ba(N<sub>3</sub>)<sub>2</sub> at 100–300 kPa and 470–530 K. The crystal structure of BaN<sub>2</sub> was again determined by powder X-ray and neutron diffraction. In contrast to the structure of SrN<sub>2</sub> which contains N<sub>2</sub> dumbbells oriented along the *c* axis and which crystallizes in the space group *I4/mmm*, the diffraction data for BaN<sub>2</sub> was more successfully refined in the space group *C2/c*. Here the octahedrally coordinated N<sub>2</sub> units are arranged perpendicular to the *c* axis and alternating by 90°. The N–N distance is almost identical to that for SrN<sub>2</sub>. Interestingly, measurements of the magnetic susceptibility indicate that the substance is metallic, which, according to simulations of the band structure, is attributed to Ba(5d)-N(2p) interactions.

### 3. Synthesis of $\gamma\text{-P}_3\text{N}_5$ in a Multianvil Press: A Compound with Tetragonal PN<sub>5</sub> Pyramids

In contrast to the diazenides P/N phases should be interpreted as covalent inorganic polymers. They are similar to B/N and Si/N compounds in that they form tetrahedral EN<sub>4</sub> units, which can be linked to give oligomeric and polymeric

networks.<sup>[15]</sup> Unlike for boron nitrides (*h*- and *c*-BN) and silicon nitrides ( $\alpha$ - and  $\beta$ -Si<sub>3</sub>N<sub>4</sub>), the structure determination of the phosphorus nitrides PN and P<sub>3</sub>N<sub>5</sub> turned out to be more difficult.<sup>[16]</sup> Thus the structure of  $\alpha$ -P<sub>3</sub>N<sub>5</sub> was first resolved in 1997 by using powder diffraction with synchrotron radiation, after a synthesis route to phase-pure samples had been developed.<sup>[17]</sup> This solid crystallizes in a novel structure type consisting of a three-dimensional network of corner- and edge-sharing PN<sub>4</sub> tetrahedra. Two fifths of the N atoms are threefold and three fifths are twofold coordinated with P atoms. The crystal structures of amorphous PN and  $\beta$ -P<sub>3</sub>N<sub>5</sub> (according to high-resolution transmission electron microscopy (HRTEM) studies an ordered stacking variant of  $\alpha$ -P<sub>3</sub>N<sub>5</sub>) are not known in detail.<sup>[15–17]</sup>

Recently, a novel high-pressure phase of phosphorus(v) nitride  $\gamma$ -P<sub>3</sub>N<sub>5</sub> was synthesized at 11 GPa and *T* = 1800 K using the multianvil technique (Figure 1; Scheme 2).<sup>[18]</sup> The



Scheme 2. Synthesis of  $\gamma$ -P<sub>3</sub>N<sub>5</sub> in a multianvil press: a) 1773 K, 11 GPa, 5 min.

compound consists of one third PN<sub>4</sub> tetrahedra and two thirds tetragonal PN<sub>5</sub> pyramids. In contrast to the  $\alpha$ -phase a larger fraction of the N atoms (i.e. four fifths) are threefold coordinated with phosphorus and only one fifth is bonded to two P atoms. Thus, starting from a  $\infty[\text{P}_3^{[4]}\text{N}_3^{[2]}\text{N}_2^{[3]}]$  network a  $\infty[\text{P}_2^{[4]}\text{P}_2^{[5]}\text{N}_2^{[2]}\text{N}_4^{[3]}]$  structure was formed (Figure 3, center). The three-coordinate N atoms are sp<sup>2</sup>-hybridized in both phases (sum of bond angles ca. 360°), while the P–N<sup>[2]</sup>–P angle of 142–171° in  $\alpha$ -P<sub>3</sub>N<sub>5</sub> decreases to 111° in  $\gamma$ -P<sub>3</sub>N<sub>5</sub>.

The most remarkable feature of the P<sub>3</sub>N<sub>5</sub> high-pressure phase is the novel PN<sub>x</sub> coordination geometry. Although distorted trigonal PN<sub>5</sub> bipyramids have been found in molecular compounds, square or tetragonal PN<sub>5</sub> pyramids were not known previously.<sup>[18]</sup> Combined with the increase of the mean coordination numbers, an increase of the average bond length is expected due to the pressure–distance rule; besides, a 32% decrease of the volume is observed. A similar increase of the coordination number combined with a

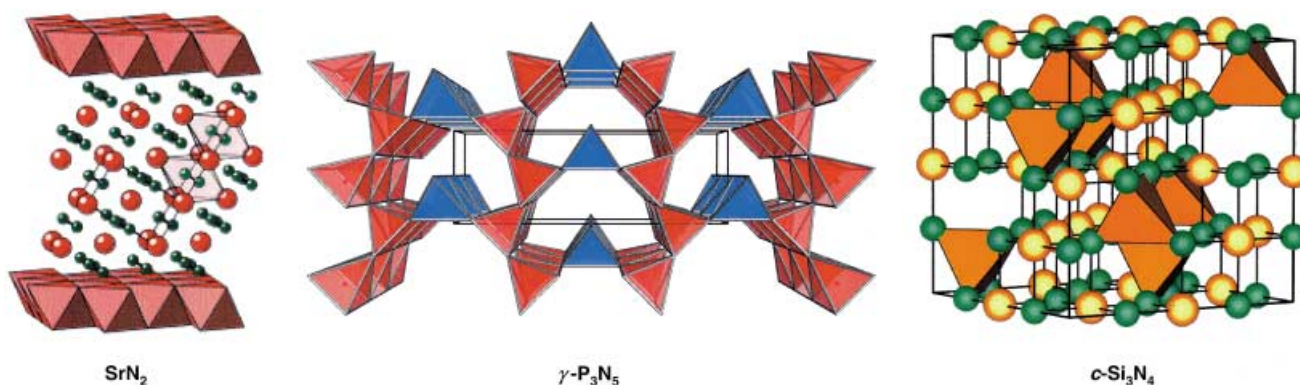


Figure 3. Left: Crystal structure of SrN<sub>2</sub>,<sup>[11]</sup> the layers at the top and bottom edges represent (N<sub>2</sub>)Sr<sub>6/3</sub> octahedra, while a ball-and-stick-illustration is used in between; red: Sr<sup>2+</sup>, green N<sub>2</sub><sup>2-</sup>. Center: Polyhedral representation of the three-dimensional network structure of  $\gamma$ -P<sub>3</sub>N<sub>5</sub>,<sup>[18]</sup> red: PN<sub>5</sub> pyramids, blue: PN<sub>4</sub> tetrahedra; right: Si<sub>3</sub>N<sub>4</sub> spinel structure<sup>[24a, b]</sup>; green: N; yellow: octahedrally coordinated Si; orange: SiN<sub>4</sub> tetrahedra.

corresponding volume decrease was found for the recently discovered high-pressure phase of  $\text{Si}_3\text{N}_4$  (see Section 4). From an initial  $\infty^3[\text{Si}_3^{[4]}\text{N}_4^{[3]}]$  network a  $\infty^3[\text{Si}_2^{[6]}\text{Si}^{[4]}\text{N}_4^{[4]}]$  structure was formed at 12 GPa and 1600 K.

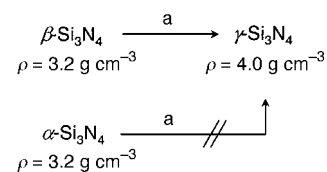
The high-pressure phases of  $\text{Si}_3\text{N}_4$  and  $\text{P}_3\text{N}_5$  are potential materials for engineering ceramics due to their temperature resistance, hardness, and chemical inertness. This statement is most likely also valid for related ternary and multinary nitride high-pressure phases such as spinel-SiAlONs<sup>[19]</sup> as well as for nitridophosphates<sup>[20]</sup> and possibly also for nitridosilicates and nitridoborates.

#### 4. Spinel- $\text{Si}_3\text{N}_4$ Synthesized by Shock-Wave Methods

Until 1999 there were six binary  $\text{EN}_x$  phases of the heavy elements of the fourth main group known:  $\alpha$ - and  $\beta$ - $\text{Si}_3\text{N}_4$ ,  $\alpha$ - and  $\beta$ - $\text{Ge}_3\text{N}_4$  as well as  $\alpha$ - and  $\beta$ - $\text{Pb}(\text{N}_3)_2$ . Additionally, certain subnitrides have been reported, which, however, are frequently amorphous and structurally not well characterized, but nevertheless are partly used as functional materials.<sup>[21]</sup> In addition, there are numerous molecular  $\text{CN}_x$  compounds known.<sup>[22]</sup> However, the existence of a hard material with the molecular formula  $\text{C}_3\text{N}_4$ , that is a carbon(IV) nitride, has not been confirmed despite several reports about its successful synthesis.<sup>[23]</sup>

In 1999 three novel spinel nitride phases of the elements Si, Ge, and Sn were discovered almost simultaneously.<sup>[24]</sup> Whereas  $c$ - $\text{Si}_3\text{N}_4$  ( $\gamma$ - $\text{Si}_3\text{N}_4$ , see Figure 3, right)<sup>[24a,b]</sup> as well as  $c$ - $\text{Ge}_3\text{N}_4$  ( $\gamma$ - $\text{Ge}_3\text{N}_4$ )<sup>[24c,d]</sup> were synthesized in diamond anvil cells and multianvil presses at  $p \geq 12$  GPa, the preparation of  $\text{Sn}_3\text{N}_4$ <sup>[24e]</sup>—the first binary Sn/N-compound—was accomplished at ambient pressure. Owing to the importance<sup>[25]</sup> of  $\beta$ -silicon nitride as a ceramic material for cutting tools, machine and engine components, as well as electronic parts, the discovery of another  $\text{Si}_3\text{N}_4$  modification attracted much interest.<sup>[26]</sup> The increase in density ( $4.0 \text{ g cm}^{-3}$ ) by about 25% compared to the formerly known modifications ( $3.2 \text{ g cm}^{-3}$ ) and a bulk modulus of about 310 GPa might indicate an application of the cubic  $\text{Si}_3\text{N}_4$  phase as a hard material. Syntheses on a larger scale than possible in diamond-anvil cells or multianvil presses are required for further characterization of the materials properties and possibly the fabrication of  $c$ - $\text{Si}_3\text{N}_4$ -based components for practical utilization. Currently, the equipment used in industry for the commercial preparation of diamond and  $c$ -BN is limited to a maximum pressure of 6 GPa,<sup>[27]</sup> which is not sufficient for the synthesis of  $c$ - $\text{Si}_3\text{N}_4$ . An alternative to static high-pressure techniques are dynamic methods, which have been used successfully to produce the ultra-hard materials  $c$ -BN and diamond.<sup>[1g,h]</sup>

Already shortly after the discovery of spinel silicon nitride Sekine et al. obtained  $c$ - $\text{Si}_3\text{N}_4$  in high yields by shock-wave methods (Scheme 3).<sup>[28]</sup> Submicrometer powders of pure  $\beta$ - $\text{Si}_3\text{N}_4$  or a  $\alpha$ -/ $\beta$ - $\text{Si}_3\text{N}_4$  mixture were blended with copper. Targets wrapped in copper or platinum hulls were cannonaded with steel or platinum projectiles.<sup>[28a]</sup> By varying the projectile velocity between 1.5 and 2.1  $\text{km s}^{-1}$  pressures of 12 to 115 GPa and temperatures above 3000 K were generated



Scheme 3. Synthesis of  $\gamma$ - $\text{Si}_3\text{N}_4$  from  $\beta$ - $\text{Si}_3\text{N}_4$  by shock-wave methods: a) 3000 K, 50 GPa, 1  $\mu\text{s}$ . The formation from  $\alpha$ - $\text{Si}_3\text{N}_4$  under the same conditions is not successful.

for about one microsecond. The products were characterized after the removal of the copper with  $\text{HNO}_3$  by X-ray structure analysis, transmission electron microscopy, and EDX. A maximum  $c$ - $\text{Si}_3\text{N}_4$  yield of 80% (!) was obtained at 50 GPa and 2400 K (decomposition of the silicon nitride was observed at still higher pressures and temperatures). The particle size of the  $c$ - $\text{Si}_3\text{N}_4$  lay between 10 and 50 nm. Interestingly,  $\alpha$ - $\text{Si}_3\text{N}_4$  does not transform into the spinel phase under the same conditions. This indicates a diffusionless (martensitic) transformation from  $\beta$ - to  $c$ - $\text{Si}_3\text{N}_4$ .

In another report from the research group of Sekine<sup>[28b]</sup> sintered dense  $\beta$ - $\text{Si}_3\text{N}_4$  discs ( $1 \times 1.2 \times 0.3 \text{ cm}$ ) were cannonaded with polycarbonate, steel, and tungsten projectiles. The minimum pressure of 36 GPa required to produce  $c$ - $\text{Si}_3\text{N}_4$  in these experiments is much higher than that for the static experiments, which is attributed to the low temperature of 460 K. A complete transformation into the high-pressure phase was not observed even at the highest pressure of 150 GPa generated in the experiments, but a 100% conversion was extrapolated for  $p_{\text{max}} = 180$  GPa. However, according to recent calculations for this pressure range, a further high-pressure modification should be formed, which is similar to the  $\text{CaTi}_2\text{O}_4$  structure, and contains  $\text{SiN}_6$  prisms as well as  $\text{SiN}_6$  octahedra.<sup>[29]</sup> Recently published diamond anvil cell studies indicate that at 34 GPa/RT a further new  $\text{Si}_3\text{N}_4$  phase already forms:  $\delta$ - $\text{Si}_3\text{N}_4$ .<sup>[30]</sup> However, the structure of this compound has not been solved so far.

A thorough design and analysis of the impact experiments allowed a determination of the pressure/density function (Hugoniot) for  $\text{Si}_3\text{N}_4$ . Using these data and the Birch–Murnaghan equation of state a value of  $300 \pm 10$  GPa was estimated for the bulk compression modulus. This result corresponds well with the results of theoretical predictions<sup>[24a]</sup> as well as recent static measurements of the compressibility of  $c$ - $\text{Si}_3\text{N}_4$  in a diamond anvil cell.<sup>[31]</sup>

#### 5. Conclusions

It is clear since the development of the ammonia synthesis and the preparation of  $c$ -BN that the application of high pressure is very useful for obtaining  $\text{EN}_x$  compounds and materials. Interesting new solids are still being synthesized by high-pressure techniques today: Kniep et al. succeeded in confirming that besides the three formerly known homopolyatomic nitrogen species  $\text{N}_2$ ,  $\text{N}_3^-$ , and  $\text{N}_5^+$  also  $\text{N}_2^{2-}$  ions are stable in the solid phase.<sup>[11]</sup> Schnick et al. demonstrated that in addition to  $\text{PN}_4$  tetrahedra also tetragonal  $\text{PN}_5$  pyramids occur as structural motifs in P–N-compounds.<sup>[18]</sup> Sekine et al. have shown that dynamic techniques may be used to produce

and characterize compounds, which are available only in very small amounts with static techniques.<sup>[28]</sup>

Another group of EN<sub>x</sub> high-pressure phases of main group elements are the nitrides AlN, GaN, and InN with rock salt structure.<sup>[32]</sup> These phases are noteworthy given the enormous interest in the corresponding Wurtzite phases for semiconductor research, and it is surprising that very little has been reported on these materials to date.<sup>[32]</sup>

Of course, the fascinating results that have been obtained recently by high-pressure techniques are not limited to binary nitrogen compounds of main group elements. For example, the discovery of a diamondlike BC<sub>2</sub>N phase, which—shortly after the structural analysis of a graphite BC<sub>2</sub>N modification obtained at 3–5 GPa<sup>[33]</sup>—was prepared in a multianvil press at 18 GPa and 2200 K, is a milestone in hard materials research.<sup>[34]</sup> This first cubic B/C/N phase now represents the second hardest substance after diamond.

Even for “simple” compounds such as elemental nitrogen, elemental carbon in the form of fullerenes, or carbon dioxide, highly interesting results were obtained upon compression in diamond anvil cells. At a pressure of 140 GPa polymeric N<sub>2</sub> was formed. The product is stable at ambient pressure up to a temperature of 100 K.<sup>[35]</sup> In a similar manner CO<sub>2</sub> was transformed at >35 GPa and 1800 K into a solid with a tridymite-like SiO<sub>2</sub> structure, which is detectable at room temperature up to a pressure of 1 GPa.<sup>[36]</sup> Depending on the *p/T* conditions, fullerenes are polymerized to give one-, two-, and three-dimensional (sometimes crystalline) networks,<sup>[37]</sup> which are characterized, for example, by very interesting magnetic properties.<sup>[38]</sup>

The examples presented here show how useful the application of high pressure is for preparative chemistry, and that the additional costs and effort can be worthwhile. Further propagation and application of high-pressure techniques will certainly produce interesting and useful materials in the future.

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