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Beryllium Nitrides at High Pressures

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Erklärung

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An expert is a person who has made all the mistakes which can be made, in a narrow field.

– Niels Bohr –

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List of Abbreviations

Alkaine Earth
Charge Distribution
Diamond Anvil Cell
Density Functional Theory
Density of States
Energy Dispersive X-ray Spectroscopy
Goodness of Fit
High-Pressure
High-Temperature
Inductively Coupled Plasma Optical Emission Spectroscopy
Infrared Spectroscopy
Laser-Heated Diamond Anvil Cell
Large Volume Press
Magic Angle Spinning Nuclear Magnetic Resonance
Nuclear Magnetic Resonance
Powder X-ray Diffraction
Single Crystal X-ray Diffraction
Scanning Electron Microscopy
Second Harmonic Generation

All figures are numbered according to the scheme

"number of chapter"." chapter-wise consecutive number",

i.e. the third figure in Chapter 2 is labelled Figure 2.3. Where reference is made to a figure in the Appendix (Supporting Information), the chapter number is retained and the letter "S" is added in front. The first figure in the Appendix belonging to Chapter 2 is therefore labelled Figure S2.1.

1. Introduction

1.1. Homage to Beryllium

Many chemists will shudder reading the caption of this chapter: "Homage to Beryllium". The 4th element in the periodic table is often referred to as the most toxic non-radioactive element.^[1] However, while the acute toxicity is actually in the same range as those of soluble Ba²⁺ salts, the acute and chronic beryllium disease, contact dermatitis and cancer are additional serious health hazards. They are caused mostly by the inhalation of Be containing dust or the contact to solvable Be salts. According to various studies, up to 16.2% of exposed workers reacts with immune response to inhaled Be particles and can evolve a pulmonary, granuloma disease, called berylliosis.^[2-4] However, mere skin contact with compounds that contain Be is not critical if the material is insoluble in water. Otherwise, many people would not be able to enjoy the minerals beryl or chrysoberyl in their colored varieties emerald, aquamarine, heliodor or alexandrite.

Reading the first paragraph of this introduction, one wonders whether mankind would not be better off by avoiding the element beryllium. After all, no useful biological function of beryllium and its compounds is known in the human body or any other living beings.^[4] Nevertheless, every year around 300 tons of elemental Be are extracted from minerals, mostly beryl and bertrandite, under strict safety precautions to avoid damage to the environment and workers.^[5] The truth is: In view of its harmful properties, it would probably already have been banned, if it had no use in which it could not be replaced. Beryllium and its compounds have unique properties and thus a wide field of applications as depicted in Figure 1.1.



Figure 1.1. A selection of applications of Be and its compounds: In fusion reactors and neutron sources (top left), in aerospace, e.g. the space shuttle, the James Webb Telescope or rockets like the Saturn V, (top right), in the alexandrite laser (bottom tight), as window material in X-ray tubes (bottom middle) and as non-magnetic and non-sparking material in tools (bottom left).^[6-13]

The most popular use of beryllium among chemists and materials scientists is as X-ray window in X-ray tubes, such as those used in diffractometers or in radiographs. The combination of the low X-ray contrast together with good mechanical properties makes beryllium suitable as a gasket material in diamond anvil cells.

While the interaction of Be with X-rays is quite small, the interaction with particle radiation such as α -particles or neutrons is large, which opens up further application possibilities: Be is an excellent neutron multiplier and a neutron source. Due to its ability to multiply neutrons according to the (n, 2n) reaction, it is foreseen as blanket material in the International Thermonuclear Experimental Reactor (ITER) in the form of Be₁₂Ti units.^[10-11]

Together with an α -particle emitter such as radium, polonium, or plutonium, Be forms a neutron source that can be used, for example, for the calibration of neutron detectors. Such a neutron source is not only mobile and long-lived, but also enabled the discovery of the neutron in 1932 by James Chadwick.^[14-15]

Outside of laboratories and devices, beryllium is also used as a construction material. In the aerospace industry, materials with the following properties are sought: High mechanical hardness and tensile strength paired with low density and low thermal expansion. A component made from such a material is lighter and at the same time more stable compared to a component made from ordinary steel. At the same time, it does not have to show any significant thermal expansion at temperatures of -243 to -220 °C in order to enable reliable operation when passing the sun. All these properties are united in the metal beryllium and make it the most suitable material for the mirror of the James Webb Telescope, launched in December 2021.^[7] In general, Be is a favored material in aerospace due to its excellent properties and has already been used in many previous missions like the Saturn rockets (tubes of Be) or the Space Shuttle (thermal protection system among others).^[6]

Tools manufactured of beryllium bronze are used for work in potentially explosive atmospheres or in areas with strong magnetic fields (e.g. magnetic resonance imaging). This alloy is non-magnetic and chips, which can occur when the tool is dropped, for example, do not cause sparks.^[12-13]

But not only beryllium as a metal and its intermetallic phases are used, but also multinary compounds with non-metal elements: The so-called alexandrite laser, a crystal of BeAl₂O₄, doped with Cr³⁺ ions, emits laser radiation with λ = 755 nm and is used for skin treatment, e.g., for the removal of tattoos. The advantage over other lasers, e.g., the ruby laser (Al₂O₃:Cr³⁺; λ = 694 nm), lies in the longer wavelength and the low interaction with the skin pigment melanin. This has the benefit that the laser radiation does not bleach the skin during treatment.^[8-9]

In all mentioned applications of beryllium and its compounds it is present as massive bulk material and not as powder or dust. Hence, the harmful potential is low due to the low biological availability. It is comparable to the usage of BaSO₄ as X-ray contrast agent, which can be injected directly into the blood of the patient. While soluble Ba salts would cause serious health problems, this is not valid for BaSO₄ due to its lack of solubility and thus, low biological availability. Same is valid for the above-mentioned gemstones like emerald, aquamarine or heliodor. However, the mechanical processing of this gemstones in workshops and the dust produced has the potential to cause the known beryllium diseases as investigated on a group of gemstone cutters in Idar-Oberstein, Germany.^[16]

In laboratories beryllium and its compounds are present as powder, soluble salts or in liquids, too. Due to the potential danger this poses, it is not a popular element to study among chemists. Only a few have the necessary courage and, in particular, the necessary equipment to perform experiments. But beryllium's exciting properties are worth it: In addition to the above-mentioned ones like low density and low thermal expansion of the metal beryllium, Be²⁺ exhibits a small ionic radius paired with a low charge. It is approx. as large as a Si⁴⁺ ion (Be²⁺: 0.27 Å; Si⁴⁺: 0.26 Å),^[17] but has half the charge. Beryllium is a strong Lewis acid and can form bonds with a high covalent character due to its high electronegativity, compared to the other elements of the 2nd main group. Furthermore, it is connected to the element aluminum by the diagonal relationship in the periodic table. This is reflected, among other things, by the fact that both hydroxides, Be(OH)₂ and Al(OH)₃, react amphoterically (Equation 1.1) in contrast to other group II hydroxides.^[18]

Be(OH)₄²⁻
$$+ 2 OH^{-}$$
 Be(OH)₂ $+ 2 H^{+}$ Be(H₂O)₄²⁺ (1.1)

Systematic research into the chemistry of beryllium-containing compounds began in the 1920s and 1930s, particularly in the field of solid-state chemistry, when the harmful properties of beryllium were not yet known.^[1] α -Be₃N₂ was synthesized by *Paulus* and *Stackelberg* in 1933.^[19] Due to its properties as a neutron multiplier (see above) and its usage in nuclear weapons, the availability of Be was strongly limited after the second world war until the end of the cold war. The research done on Be compounds was performed mostly in national research agencies, like the Los Alamos National Laboratory. The results of this research are accessible to the public today, e.g. in form of handbooks.^[20-21] But there have also been some discoveries in public research. This included the work of *Eckerlin* and *Rabenau* on β -Be₃N₂ and BeSiN₂.^[22-23] When the restrictions were relaxed, the discovery of the hazard of Be containing compounds slowed down the research, again.^[1] However, slowly starting around 2005, research on beryllium and its compounds has been picking up speed. Especially in the field of solid-state chemistry, systematic research began in 2010, to explore the usage of Be-containing networks for LED phosphors. In fact, many new compounds have been discovered, e.g. SrLi₂[Be₄O₆]:Eu²⁺, Sr[Be₆ON₄]:Eu²⁺, SrBeO₂:Eu²⁺ or BaBeSiON₂:Eu²⁺ which show excellent properties for use in phosphor converting-LEDs (pc-LEDs).^[24-27]

It is apparent that the class of beryllium-containing compounds is a highly diverse one regarding its properties and potential field of applications. However, especially the classes of beryllium nitrides and nitridoberyllates are sparsely investigated, although we can expect a variety of new compounds with unique structures and interesting properties. This thesis therefore aims to address the deficits in fundamental research on beryllium nitrides and to open new classes of substances using innovative synthesis methods. The following chapters give a summary of known ternary beryllium nitrides and their structural chemistry and deal with the question, why is it a promising idea to combine beryllium and nitrogen (Section 1.2), as well as with the challenging synthesis of Be-N compounds and general problems in structure elucidation (Section 1.3). Section 1.4 focuses on the previously known compounds synthesized under high-pressure conditions, and why it is a favorable approach to introduce pressure as an additional reaction parameter. Section 1.5 provides a brief overview of state-of-the-art high-pressure techniques, which were used in the course of this work. Finally, Section 1.6 outlines the scope of this thesis.

1.2. Beryllium Nitrides and their Structural Chemistry

Two terms are used frequently in the following and throughout this work, which is why they are clearly defined here: Beryllium nitride and nitridoberyllate. The former describes the combination of beryllium and nitrogen in a compound consisting of Be^{2+} and N^{3-} ions and is therefore more general. This term is also used for neutrally charged networks and double nitrides. The term nitridoberyllate is used for compounds that contain an anionic Be-N network whose charge is balanced by counter cations such as Ca^{2+} , Sr^{2+} or Ba^{2+} . The nomenclature is based on Liebau's classification of silicate minerals.^[28]

Before understanding the structural chemistry of beryllium nitrides, it is recommended to take a step back and to analyze the structural relationship between oxoberyllates and oxosilicates. Due to the similar ionic radii of Be²⁺ and Si⁴⁺ (Be²⁺: 0.27 Å; Si⁴⁺: 0.26 Å),^[17] it is possible to build up beryllate structures analogous to the versatile class of silicates, following the isolobal concept. Starting, e.g. from Mg₂SiO₄ (olivine), the Si position can be substituted by Be²⁺. To compensate the charge deficit, two counter cations with a formal charge of 3+ could substitute the Mg atoms, for example Al³⁺, forming the naturally occurring Al₂BeO₄ (chrysoberyl), or Cr³⁺ as found in synthetic Cr₂BeO₄.^[29-30]

In order to compare different compounds, it is necessary to analyze how interwoven the network is, that forms the structure. A simple measure of this is the degree of condensation: It is defined by the ratio of tetrahedral centers (*T*) to ligands (*X*) ($\kappa = N(T)/N(X)$). The maximum degree of condensation for the classes of oxosilicates and oxoberyllates is present in the respective binary compounds, i.e. ½ in SiO₂ and 1 in BeO. Incorporating Be in a silicate network, κ can be increased, for example in the natural mineral phenakite, Be₂SiO₄ leading to $\kappa = \frac{3}{4}$.^[31] Increasing the degree of condensation can improve the rigidity of the network and thus the mechanical properties of the compound and lead to interesting structural motifs, among other things, but is also advantageous in the development of LED phosphors.^[24, 32-33]

Another successful approach to increase the degree of condensation in the class of silicates is to replace oxygen with nitrogen, creating the so-called class of nitridosilicates. The respective binary compound is Si₃N₄, increasing the degree of condensation of former $\kappa = \frac{1}{2}$ to $\kappa = \frac{3}{4}$. But why can nitridosilicates be more condensed than oxosilicates? In an oxosilicate, the most common building block, SiO₄ tetrahedra, can only be connected via shared vertices on two sides. Edge-sharing is not possible due to the Coulomb repulsion of the two Si⁴⁺ ions, which would come very close to each other in such a geometry. The substitution of O²⁻ by N³⁻, however, leads to a better shielding of the Si⁴⁺ ions between themselves and enables the linking via edges, e.g. in BaSi₇N₁₀.^[34] Furthermore, multi-bridging anions like N^[3] or N^[4], found in *AE*YbSi₄N₇ (*AE* = Sr, Ba) are possible.^[35]

As mentioned above, the Be²⁺ cation has almost the same ionic radius as Si⁴⁺, but half the charge. As a result, Be²⁺ needs no additional shielding to enable edge-sharing tetrahedra and multi-bridging ligands such as O^[3] or even O^[4]. Hence, these structural motifs can not only occur in nitridosilicates but also in oxoberyllates. Respective isostructural frameworks can be found between these two compound classes, e.g. SrBe₃O₄ and SrBeSi₂N₄,^[36-37] NaSbBe₄O₇ and *AE*YbSi₄N₇,^[35] β -SrBeO₂ and closely related *AE*SiN₂ (*AE* = Sr, Ba),^[25, 38] as well as BeGa₂O₄ and β -Si₃N₄.^[39-40]

This relationship between the charge of the central atom of the tetrahedron and the ligand in relation to the degree of condensation is important to understand. Replacing oxygen by nitrogen in

a beryllate network, the degree of condensation can be increased to a value of $\kappa = 1.5$ in Be₃N₂. This high degree of condensation is reflected in a structure in which BeN₄ tetrahedra are linked to each other via three edges. The nitrogen atoms are surrounded by six Be atoms, forming NBe₆ octahedra.^[19] This unusually high degree of condensation of 1.5 is the highest value that can be achieved in a nitride network, which is built up from tetrahedra. Accordingly, we can expect the class of nitridoberyllates to produce structures and networks that will not be comparable to those of silicates or nitridosilicates and will therefore form unknown structural motifs.

However, the prospect of new, fascinating structures is not the only reason to combine beryllium and nitrogen in a compound. More reasons become apparent, when comparing beryllium with its next neighbors in the periodic table: Its electronegativity is approx. 60% higher compared to lithium (Li: 0.98; Be: 1.57, Pauling scale).^[41] Moreover, the first ionization energy is even higher than the one of boron. Hence and as mentioned in Section 1.1, Be has a tendency to form bonds of a high covalent character to nitrogen, especially in comparison to oxygen. The formation of 3D networks with this kind of bonding makes them more rigid and more resistant to external mechanical influences, which is reflected in a high bulk modulus or increased Vickers hardness, among other things. Examples of covalent bonded networks with excellent mechanical properties are diamond or BC₂N.^[42-43]

The above-mentioned properties make beryllium interesting for phosphor research. Hence, the research of beryllium nitrides was mostly driven by solid state lighting. Especially the substance class of *AE*-Be-N (*AE* = Ca, Sr, Ba) attracted interest due to the possibility of replacing AE^{2+} with Eu²⁺ ions.^[37, 44-46]

н]																He
Li	Be											В	С	N	0	F	Ne
Na	Mg											Al	Si	Ρ	S	Cl	Ar
к	Ca	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Υ	Zr	Nb	Mo	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	I	Xe
Cs	Ва	La	Hf	Та	W	Re	Os	lr	Pt	Au	Hg	ΤI	Pb	Bi	Ро	At	Rn

Figure 1.2. Periodic table of elements with none (white), one (red), or two (green) ternary beryllium nitrides.

Figure 1.2 shows that, in general, sparsely is known about ternary beryllium nitrides. At the moment of this thesis, only eleven ternary compounds have been discovered. For the reasons mentioned above, the best studied class is *AE*-Be-N, represented by two formula types, namely *AE*Be₂N₂ (AE = Mg, Ca, Sr, Ba)^[45-46] and *M*Be₂₀N₁₄ (*M* = Sr, Ba, Eu).^[44] In the first and fourth main group, one compound exists each, namely LiBeN and BeSiN₂.^[22, 47] BeP₂N₄ and its high-pressure polymorph spinel-type BeP₂N₄ represent the only two members in the fifth main group.^[48-49] For all other groups in the periodic table, no ternary beryllium nitride has been published so far. Especially, the absence of any transition metal beryllium with every transition metal beside Zn, Cd and Hg.^[50-54]

At this point it is worth mentioning that overall more compounds containing beryllium have been synthesized, for example quaternary nitridoberyllates like $AEBeSi_2N_4$ (AE = Ca, Sr, Ba) or such with nitrogen and oxygen, for example BaBeSiN₂O.^[26, 37] However, if so little is known about a system, it is useful to investigate the reaction behavior, structural influence and bonding situation in compounds with a limited number of elements. The complexity and number of chemical influences increases with the number of elements in a compound. Therefore, the focus in this thesis is on ternary compounds.

However, this makes no difference to the description of the structural motifs in nitridoberyllates, as they are equivalent in ternary and quaternary compounds. In contrast to nitridosilicates, which are mostly built up from SiN₄ tetrahedra, there are two common building blocks for nitridoberyllates, namely trigonal planar BeN₃ units and BeN₄ tetrahedra (Figure 1.3). Given the limited number of compounds, it is not possible to classify when BeN₃ or BeN₄ units are preferred. BeN₃ units occur in the form of edge-sharing layers in *AE*Be₂N₂ (*AE* = Ca, Sr, Ba) or LiBeN.^[45, 47] Vertex-sharing tetrahedra networks occur in BeSiN₂, networks formed by edge-sharing tetrahedra can be found in MgBe₂N₂ or *M*Be₂₀N₁₄ (*M* = Sr, Ba, Eu).^[44-45] Mineral-analog structures are found in phenakite-type BeP₂N₄ (phe-BeP₂N₄), while isolated BeN₄ tetrahedra are present in the high-pressure polymorph spinel-type BeP₂N₄.^[48-49] The structural motif of BeN₆ octahedra exists so far in only one compound, namely in the polynitride BeN₄, which was synthesized in a diamond anvil cell at 84 GPa (Figure 1.3).^[55]



Figure 1.3. The individual coordination polyhedra (A) can be linked in different ways: In layers of edge-sharing BeN₃ units as in SrBe₂N₂, in layers of edge-sharing tetrahedra as in MgBe₂N₂ or as a 3D network via corner sharing (BeSiN₂) or edge sharing (SrBe₂₀N₁₄). Isolated tetrahedra are also possible as in spinel-type BeP₂N₄. BeN₆ octahedra are linked by polynitride anions in BeN₄. Cations are shown in orange (Mg, Sr) or purple (P) or have been omitted for better clarity. Be: green, N: blue.^[22, 44-45, 48, 55]

A look at the structures of the compounds known to date shows that, in addition to silicate-like compounds, significantly more highly condensed networks can be synthesized. By the combination of Be and N, it is theoretically possible to create a variety of structures that exceed the versatile class of silicates. The challenges involved in synthesizing this diverse class of structures are discussed in the next section.

1.3. Synthesis and Characterization of Beryllium Nitrides

Section 1.1 and 1.2 depicted why it is a promising idea to combine beryllium with nitrogen in nitride compounds, what different applications and structural features can be expected. This section deals with the challenges in the synthesis and characterization of beryllium nitrides.

In geochemistry, Be is categorized as a lithophile element according to the Goldschmidt classification.^[56] The phrase "lithophile" is derived from the Greek word "lithos" (stone) and "philos" (beloved) and is used for elements that like to form minerals and stones with oxygen and remain in the earth's crust. This affinity of beryllium for oxygen also holds for synthetic materials. Hence, the meticulous exclusion of oxygen during the synthesis process is very important and can be achieved by state-of-the-art glovebox and Schlenk technique. Even traces of oxygen lead to the formation of BeO or, depending on the level of contamination, oxonitridoberyllates or oxoberyllates.^[26-27]

In the sole presence of nitrogen, Be_3N_2 is the thermodynamic stable and preferred phase. Its standard enthalpy of formation with $\Delta H_f^0 = -588$ kJ/mol is the highest among main group nitrides, even higher than the one of AIN ($\Delta H_f^0 = -318$ kJ/mol).^[18, 57] According to this, Be_3N_2 is very stable and therefore less reactive and difficult to activate. Of course, it is also possible to use other precursors, e.g. elemental Be or beryllium halides. However, the first is very difficult to process due to its high hardness and its surface often passivated with a layer of $Be(OH)_2$ and the latter is very sensitive to hydrolysis, in parts too reactive and not suitable for every synthesis mode due to the release of hydrogen halides.^[18] The phrase "too reactive" means, that a synthesis is best carried out under controlled conditions and should not take place when mixing the reactants in a mortar. Moreover, it is recommended to only use the desired elements in the starting materials to minimize the formation of unwanted side phases. The most favored precursor uniting Be and N, $Be(N_3)_2$ is not applicable due to its high sensitivity and health hazards resulting from a spontaneous explosion.^[58-61]

For the reasons stated above, Be_3N_2 or elemental Be are the favored starting materials for nitride synthesis. Nevertheless, both are difficult to activate in a reaction. The latter can even be heated until red heat under water without any reaction due to the above-mentioned passivation.^[18] For the activation of these two materials, two main strategies have been developed in the past: First, the reaction with very reactive reactants such as Li₃N and second, the thermal activation of Be₃N₂ under high-temperature conditions in a radio-frequency furnace, or the combination of both. The different synthesis methods are explained below on the example of LiBeN, BeSiN₂ and SrBe₂₀N₁₄.^[22, 44, 47]

LiBeN is synthesized by the reaction of Li_3N with elemental Be at a temperature of 1275 K (Equation 1.2).^[47] At these temperatures, Li_3N is present as melt and can activate the Be metal.

 $\label{eq:list} \begin{array}{ll} \text{Li}_3\text{N} + \text{Be} \rightarrow \text{Li}\text{BeN} + 2 \mbox{Li} & (1.2) \\ \\ \text{Be}_3\text{N}_2 + \text{Si}_3\text{N}_4 \rightarrow 3 \mbox{BeSiN}_2 & (1.3) \end{array}$

In the synthesis of BeSiN₂ from Be₃N₂ and Si₃N₄, no reactive reactant is present (Equation 1.3). Both binary nitrides exhibit a melting point > 2000 °C. The synthesis conditions reported in the literature only indicate a required temperature of over 1800 °C for a successful synthesis.^[22] Among other

things, the exact synthesis conditions of this reaction are examined in Chapter 3 and, without getting too far ahead of ourselves, the findings from the literature can be confirmed at this point: No significant conversion can be observed up to 1750 °C, a quantitative reaction takes place at temperature > 1900 °C.

The two presented synthesis routes can be combined to find a compromise between the reactivity of the starting materials and the synthesis temperature. For example, $MBe_{20}N_{14}$ (M = Sr, Ba, Eu) can be synthesized from $M(NH_2)_2$ or M_2N and Be_3N_2 in a radio-frequency furnace at a moderate temperature of 1400 °C.^[44]

However, if temperature-labile starting materials such as P_3N_5 are to be reacted with the unreactive Be_3N_2 , modified synthesis conditions like pressure stabilization are necessary. As this is a core topic of this thesis, it is introduced in detail in Section 1.4.

The analysis and identification of potential new beryllium nitrides presents some challenges. As mentioned in Section 1.1, Be metal is used as X-ray window due to its low interaction with X-rays. This advantage for the application turns out to be a disadvantage in the analysis by means of X-ray diffraction methods such as single crystal X-ray diffraction (sc-XRD). Due to the low atomic form factor of Be, high-angle data is necessary, which in turn requires crystals of sufficiently good quality for in-house analysis or an X-ray source with high flux as can be found at synchrotron facilities. Despite these possibilities, the analysis with XRD methods is not always unambiguous. Fortunately, ⁹Be is an isotope, which is sensitive to nuclear magnetic resonance (NMR) spectroscopy and has a natural abundance of almost 100%. Since ⁹Be is a nucleus with quadrupole moment, NMR analysis is very sensitive to distortions of the local geometry or changes in the coordination polyhedron. Thus, trigonal planar BeN₃ units can be clearly distinguished from BeN₄ tetrahedra by the NMR spectrum. Unfortunately, there are no comparative values for BeN₄ tetrahedra yet, which is why this thesis also deals with the investigation of Be in a tetrahedral nitrogen environment for the first time.

The combination of XRD and NMR methods is always useful for Be-containing solids. If in doubt, further analytical methods such as additional chemical analysis like inductively coupled plasma optical emission spectroscopy (ICP-OES) are recommended. Common methods like energy-dispersive X-ray (EDX) spectroscopy usually do not detect beryllium, but can still be used to exclude impurities. The refined structural model can be checked using second harmonic generation (SHG) or Raman measurements combined with density functional theory (DFT) calculations. The validation of results from XRD analyses is important for all solid-state chemists. In particular, it is essential for compounds that contain beryllium, as the structural model derived from XRD data is not always unambiguous.

1.4. Beryllium Nitrides at High Pressures

As covered in Section 1.2, the number of investigated ternary beryllium nitrides is very limited. In addition to the health harming properties as depicted in Section 1.1, the challenging synthesis conditions as listed in Section 1.3 could be one reason for this small number of compounds. Hence, the pressure stabilization of thermal labile staring materials could be a suitable approach to circumvent synthetic barriers.

However, just as for the ambient pressure methods, sparsely is known about Be and its compounds under high-pressure conditions. So far, mainly the high-pressure behavior of Be-containing minerals or other oxidic systems was investigated. For example, the mineral hurlbutite, CaBe₂(PO₄)₂, was examined under high-pressure conditions, elucidating several phase transitions.^[62] The modification at the pressure of 89 GPa exhibits not only PO₆ but also BeO₆ octahedra. Most recently, BeCO₃ was synthesized in a calcite-type modification, which also consists of BeO₆ octahedra, already at a synthesis pressure of approx. 40 GPa.^[63] This example in the oxygen system demonstrates, high-pressure conditions are a suitable approach for the synthesis of so far uncommon structural motifs.

Despite the lack of knowledge for beryllium nitrides, *Pucher et al.* could demonstrate on the example of phe-BeP₂N₄ a high-pressure synthesis of a beryllium nitride at 5 GPa and 1500 °C in a Large Volume Press (LVP).^[49] What is remarkable about this synthesis is the combination of the temperature labile P₃N₅ and the refractory Be₃N₂. P₃N₅ starts to decompose at 850 °C, forming PN and N₂.^[64] According to the principle of Le Chatelier, applying pressure can reduce the decomposition to a minimum and give access to high-temperature synthesis, as they are needed for beryllium nitrides (see Section 1.3). Of course, this pressure-induced stabilization also holds for the respective metal nitride, here Be₃N₂. Hence, for the synthesis of other P-N compounds, the so-called azide route is an established approach to provide more reactive reactants, for example $AE(N_3)_2$ for AEP_2N_4 (AE = Ca, Sr, Ba).^[65] As mentioned earlier, this approach is not feasible for Be, because in the case of a decomposition of the unstable and sensitive Be(N₃)₂, finely dispersed Be dust could cause serious health problems in addition to injuries caused by the explosion.^[58, 60]Therefore, a compromise between pressure stabilization of P₃N₅ and high-temperature activation of Be₃N₂ must be found as shown on the example of phe-BeP₂N₄.

Once a stable ternary compound is formed, it is a suitable candidate for further high-pressure investigations. *Vogel et al.* examined the high-pressure behavior of single crystals of phe-BeP₂N₄ in a diamond anvil cell (DAC) at a pressure of 47 GPa. They observed a phase transition to spinel-type BeP_2N_4 (sp-BeP₂N₄), which consists of PN₆ octahedra as well as BeN_4 tetrahedra (Figure 1.4). This new modification was quenchable to ambient pressure conditions, afterwards.^[48]



Figure 1.4. Beryllium nitrides synthesized under high-temperature high-pressure conditions with their synthesis pressure: phe-BeP₂N₄ (left), sp-BeP₂N₄ (middle) and BeN₄ (right).^[48-49, 55] Be: green, P: violet, N: blue.

The so far only compound exhibiting BeN₆ octahedra is the polynitride BeN₄ (Figure 1.4). It was synthesized by *Bykov et al.* in a DAC at a pressure of 84 GPa starting from Be and N₂. Its structure is isostructural to FeN₄ and is built up from BeN₆ octahedra, which are connected via [N₂] units. In their work, also the high-pressure behavior of Be₃N₂ was investigated: The ambient-temperature modification α -Be₃N₂ is at least stable in its anti-bixbyite modification until 60 GPa, even upon laser-heating. This underlines the high stability of this binary compound.^[55]

To the start of this thesis, only these three beryllium nitrides are known to be synthesized under high-pressure conditions. Nevertheless, this small number already shows that the introduction of the reaction parameter pressure is a promising idea: Temperature-labile starting materials can be stabilized enabling their use as reactants before decomposition, at least in the case of P_3N_5 . Pursuing this approach, some white spots on the map of ternary beryllium nitrides could be eliminated. In addition, the synthesis of the polynitride BeN₄ demonstrates that the results from mineral research can be transferred to the nitride system regarding the geometry of BeN₆ octahedra.

Experiments can be carried out under high-pressure conditions utilizing a large volume press as well as diamond anvil cells among others. Both techniques were used in this thesis and are therefore described in more detail in the next section.

1.5. State of the Art High-Pressure Techniques

Various experimental setups are available for carrying out reactions under high-pressure and high-temperature conditions. The most common techniques are the belt apparatus, the Piston cylinder, the Paris-Edinburgh press and the multi anvil press.^[66-69] Each of these presses has different advantages and disadvantages in terms of achievable pressure, sample volume, pressure distribution and cost per batch. The multi anvil press technique is characterized in particular by a relatively isostatic pressure distribution with a sample volume that is not too small, so that sufficient product can be isolated to perform analysis on the bulk material and not just on single particles. For this reason, the term large volume press (LVP) is also used in the following.



Figure 1.5. Walker-type large volume press (A), which exerts uniaxial pressure on the Walker module (B). The tungsten carbide cubes (C) are arranged in the center of the module. The truncated edges of the WC cubes form a cavity for the octahedron, which in turn consists of several components (D & E).

Today's form of modern multi anvil presses were introduced by *Kawai* and *Endo* and modified by *Walker* (Figure 1.5A).^[70-71] The uniaxial force is transferred in several steps and several pressure-transmitting units (multi anvil) to the surface of an octahedron. As a result, the pressure distribution becomes more isostatic and the pressure increases as the area shrinks over different anvils: First, the uniaxial pressure from a machine press is transferred by six wedges to the geometry of a cube (Figure 1.5B). This cube consists of six small tungsten carbide cubes, which have truncated corners. If the cubes are arranged in such a way that all truncated corners point to the center, a cavity in the form of an octahedron is created (Figure 1.5C). To prevent the cubes from contacting each other, they are separated by pyrophyllite gaskets. In the created cavity a MgO octahedron is placed. The ratio of the area of the truncated cube corners and the size of the octahedron determines the

maximal pressure. In the course of this thesis, syntheses up to a pressure of 9 GPa were conducted in the large volume press and the 18/11 assembly was used for this purpose. 18/11 refers to the edge length of the octahedron of 18 mm and the length of the truncated corner of 11 mm. The maximum pressures that can be achieved by using the technology of a multi anvil press are up to 100 GPa. However, such high pressures can only be achieved by using much smaller octahedra and thus reducing the sample volume and using other cube materials such as sintered diamond.^[72] The sample itself is located inside the octahedron, which is built up as follows: The starting materials are packed inside a BN-crucible with a lid. The crucible is placed in a cylinder, which is made from graphite and acts as a resistance heater. MgO discs are used as spacers to place the sample in the center of the graphite cylinder. The furnace is contacted with Mo disks. This setup is placed in a ZrO₂ cylinder, which in turn is glued into the octahedron (Figure 1.5D and 1.5E). Finally, the octahedron is placed in the above-mentioned cavity and the whole assembly is transferred to the large volume press. The experimental designs are described in detail in Chapters 2–4 and in the corresponding Supporting Information (Section 7.1–7.3). Furthermore, detailed descriptions can be found in the literature.^[73]



Figure 1.6. Schematic structure of a diamond stamping cell (A) and photo of a sample chamber of a DAC with two crystals as sample, tungsten piece and ruby splitter (B). Depending on the diamond shape, different pressures can be achieved (C).

If the pressure needs to be even higher and *in-situ* investigation such as X-ray diffraction with simultaneous heating are required, diamond anvil cells (DAC) are the method of choice. As the name suggests, diamonds rather than tungsten carbide cubes are used as anvils here. On the one hand, diamonds exceed the mechanical stability of other materials like tungsten carbide, and, on the other hand, they are transparent to a wide range of the electromagnetic spectrum and thus enable *in-situ* investigations. There exist different designs of diamonds, depending on the desired pressure range (Figure 1.6): Flat culet diamonds allow a pressure up to approx. 150 GPa, while with single- or

double-bevel diamonds pressures up to 400 GPa can be achieved.^[74] With the introduction of toroidal and double stage diamonds the benchmark of 1000 GPa was broken for the first time.^[75-76]

The progress that has been made in this field of research over the past decades is remarkable. The technology of diamond anvil cells can therefore not only be used to open up new areas of chemistry, but much effort is also being carried out on the technology itself in order to continuously develop it further. During this thesis, flat culet diamonds with the Boehler-Almax design were used to achieve pressure of up to 120 GPa.^[77] For this purpose, the diamonds were fixed to seats made of tungsten carbide and equipped with a previously laser-drilled rhenium gasket. In addition to the sample, the DAC is filled with a pressure marker (a piece of ruby, gold or tungsten, Figure 1.6) and a pressure transmitting medium (for example Ne or N₂). Like the assembly of the cubes in the large volume press, the diamonds must not touch each other to avoid their breakage. By bringing the diamonds closer together, e.g. by tightening the screws of the cell, the pressure inside the DAC increases. Experimental details on the individual experiments can be found in Chapters 3 and 5 as well as in the corresponding Supporting Information (Section 7.2 and 7.4).

1.6. Scope of this Thesis

Previous research in the field of beryllium nitrides was mostly driven by the motivation of new host materials for solid state lighting. The scope of this thesis is to synthesize new ternary beryllium nitrides, to open new compound classes and to systematically expand our understanding of beryllium nitrides. In particular, the application of the method of high-pressure synthesis, which has so far only been used for BeP_2N_4 , is being further developed. Initially, the existing system of Be-P-N compounds is extended by the synthesis of Be_2PN_3 to gain access to wurtzite-type, highly condensed beryllium nitrides. In addition, the first NMR-experiments on ⁹Be in a tetrahedral nitride coordination are conducted to set the basis for further investigations (Chapter 2). Building on this, the previously gained knowledge is used to open the substance class of Be-Ge-N for the first time with the synthesis of BeGeN2. This new compound will be compared with its lighter homologue BeSiN₂ in order to investigate differences in synthesis, structure and properties (Chapter 3). With the subsequent synthesis of $W_2Be_4N_5$ and $W_4Be_8N_9$, not only the substance class of Be-W-N is opened, but it also creates a starting point for the further exploration of transition metal beryllium nitrides (Chapter 4). Finally, with the synthesis of $BeW_{10}N_{14}(N_2)$, the very first ternary transition metal compound containing [N₂] units is successfully prepared and, in addition, the sought-after motif of BeN₆ octahedra in a nitride is confirmed (Chapter 5).

1.7. References

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2. Highly Condensed and Super-Incompressible Be_2PN_3

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Abstract: Although beryllium and its compounds show outstanding properties, owing to its toxic potential and extreme reaction conditions the chemistry of Be under high-pressure conditions has only been investigated sparsely. Herein, we report on the highly condensed wurtzite-type Be_2PN_3 , which was synthesized from Be_3N_2 and P_3N_5 in a high-pressure high-temperature approach at 9 GPa and 1500 °C. It is the missing member in the row of formula type M_2PN_3 (M = Mg, Zn). The structure was elucidated by powder X-ray diffraction (PXRD), revealing that Be_2PN_3 is a double nitride, rather than a nitridophosphate. The structural model was further corroborated by ⁹Be and ³¹P solid-state nuclear magnetic resonance (NMR) spectroscopy. We present ⁹Be NMR data for tetrahedral nitride coordination for the first time. Infrared and energy-dispersive X-ray spectroscopy (FTIR and EDX), as well as temperature dependent PXRD complement the analytical characterization. Density functional theory (DFT) calculations reveal super-incompressible behavior and the remarkable hardness of this low-density material. The formation of Be_2PN_3 through a high-pressure high-temperature approach expands the synthetic access to Be-containing compounds and may open access to various multinary beryllium nitrides.

Beryllates are a class of compounds of great structural diversity, owing to the flexibility of the coordination of beryllium, ranging from trigonal planar units to corner- and edge-sharing tetrahedra.^[1-3] Due to the similar ionic radii of Be²⁺ (0.27 Å) and Si⁴⁺ (0.26 Å),^[4] it is even possible to build up structures analogous to the versatile class of silicates, following the isolobal concept: Starting e.g., from Mg₂SiO₄ (olivine), the Si position can be substituted by Be²⁺. To compensate the charge deficit, two counter cations with a charge of 3+ could substitute the Mg atoms, for example Al³⁺, forming naturally occurring crysoberyl Al₂BeO₄ or Cr³⁺ as found in synthetic Cr₂BeO₄.^[5-6]

To describe how interwoven a network is, the degree of condensation κ is an appropriate measure: It is defined by the ratio of tetrahedral centers (*T*) to ligands (*X*) ($\kappa = N(T)/N(X)$). The maximum degree of condensation is present in the respective binary compounds, for example ½ in SiO₂ and 1 in BeO. Incorporating Be in a silicate network, κ can be increased, for example in the natural mineral phenakite, Be₂SiO₄ leading to $\kappa = \frac{3}{4}$.^[7] Starting from this mineral, the isolobal concept can be used again: If the Si position is substituted by Be²⁺ and the O atoms are replaced by N, the former Be position may be substituted by P⁵⁺ to regain charge neutrality. This procedure leads to a sum formula of BeP₂N₄ and, actually, phe-BeP₂N₄ and its high-pressure polymorph spinel-type BeP₂N₄ (sp-BeP₂N₄) are the only known beryllium phosphorus nitrides, so far.^[8-9] The class of phosphorus nitrides is also closely related to the silicates due the isolobal relationship between Si–O and P–N. Hence, nitridophosphates and silicates form related structures, for example *M*P₂N₄ (*M* = Ca, Sr, Mn, Cd) crystallizing in the megacalsilite (KAISiO₄)-type.^[10-11]

Most recently, nitridophosphates with a lower P content were the focus of research, giving *in-situ* insights into the reaction mechanism of the ternary wide band gap semiconductor Zn_2PN_3 .^[12] Moreover, they show versatile properties: $Li_{12}P_3N_9$ and its high-pressure polymorph Li_4PN_3 were discussed as Li-ion conductors, Ca_2PN_3 shows a broad-band red emission upon doping with Eu^{2+} -ions and was a model compound for new synthetic methods using a Hot Isostatic Press.^[13-14] The wide band gap materials Zn_2PN_3 and Mg_2PN_3 show potential for their application in power electronic devices or photovoltaic cells.^[15] Just as with the nitridophosphates with a higher P content, the structures are related to the ones of oxosilicates: Li_4PN_3 and Zn_2PN_3 are classified as catena-nitridophosphates due to their similarity to inosilicates. Mg_2PN_3 and Zn_2PN_3 crystallize in a distorted wurtzite-type structure, which is also related to silicates (Li_2SiO_3 -type).^[16] Remarkably, Mg_2PN_3 and Ca_2PN_3 can be synthesized at low pressure conditions from the binary nitrides.^[17] However, this

synthesis route does not seem feasible for highly condensed Be-containing phosphorus nitrides. The reason can be found in the difference between the most common starting materials: While Be_3N_2 is stable up to temperatures of 2200 °C and is used as a refractory ceramic, P_3N_5 starts to decompose at 850 °C, forming PN and N₂.^[18-19] According to the principle of Le Chatelier, applying pressure can reduce the decomposition to a minimum and give access to high-temperature synthesis. Of course, this pressure-induced stabilization also holds for the respective metal nitride. Hence, the most common approaches start from the more reactive metal azide in combination with P_3N_5 . However, this route is in the case of Be not feasible as well: $Be(N_3)_2$ is extremely unstable and sensitive due to its covalent bonding character, and more challenging in synthesis and handling than $AE(N_3)_2$ (AE = Ca, Sr, Ba).^[20-24] Additionally, in case of a decomposition by accident, the inhalation of finely dispersed Be dust, could cause serious health problems.^[25-26] Therefore, a compromise between pressure stabilization of P₃N₅ and thermal activation of Be₃N₂ must be found as shown in the synthesis of phe-BeP₂N₄ at 5 GPa and 1500 $^{\circ}$ C.^[8] To gain access to even more highly condensed compounds, more extreme conditions such as higher pressure has to be applied. Although the research on Be chemistry is challenging, it is worth it, not only because of the structural diversity, but also because of the outstanding properties of Be-containing compounds like refractory behavior, exceptional ultra-incompressibility like in sp-BeP₂N₄ or high thermal conductivity coinciding with high dielectric properties at high temperature conditions, as found in BeO.^[9, 27-28]

In this contribution, we present Be_2PN_3 – the missing member in the row of the ternary nitrides M_2PN_3 (M = Mg, Zn).^[17, 29] According to Equation 2.1, the title compound was synthesized starting from stoichiometric amounts of Be_3N_2 and semi-crystalline P_3N_5 under high-pressure (HP) high-temperature (HT) conditions.

$$2 Be_3N_2 + P_3N_5 \to 3 Be_2PN_3$$
 (2.1)

The starting materials were finely ground, packed into an *h*-BN crucible, compressed to 9 GPa and heated to 1500 °C in the large volume press, obtaining a colorless powder. The as-synthesized sintered powder can scratch tungsten carbide mortars and contains crystals up to 3 μ m length, as shown in Figure 2.1. Milder reaction conditions (< 9 GPa) result in the formation of BeP₂N₄ and Be₃N₂. More detailed information on the HP/HT synthesis of Be₂PN₃ can be found in the Supporting Information.



Figure 2.1. Exemplary SEM image of crystals of Be₂PN₃. Crystals are up to 3 µm in length and width.

Single-crystal XRD measurements of Be₂PN₃ were not feasible due to the small crystal size. Hence, the crystal structure of Be₂PN₃ was solved and refined from X-ray powder diffraction data based on the structural model obtained after indexing and Charge Flipping. Be₂PN₃ crystallizes in a wurtzite-type structure (*Cmc*2₁ (no. 36), *a* = 8.4610(16), *b* = 4.8777(6) and *c* = 4.5691(8) Å, Z = 4, more details in the Supporting Information).^[30] No evidence of mixed occupancy was detected. The refined crystal structure and coordination polyhedra of Be and P are illustrated in Figure 2.2 and 2.3. Geometry relaxation from DFT calculations of the structure supports the stated model by only a small shift of the atomic positions (see Table S2.6).



Figure 2.2. The crystal structure of Be_2PN_3 consists of all-side corner-sharing BeN_4 (green) and PN_4 (brown) tetrahedra (N: blue). Viewed along [001] the wurtzite-type structure becomes apparent.



Figure 2.3. Coordination polyhedra of Be1 and P1.

Compared to Mg₂PN₃, the distortion of the structure in relation to the ideal wurtzite-type is far lower due to more similar distances between Be-N and P-N in contrast to Mg-N (see Figure S2.3). The structure is built of regular and all corner-sharing BeN₄ and PN₄ polyhedra. With respect to the entire four-fold coordination of Be and P, Be₂PN₃ can be classified as a double nitride rather than a beryllium nitridophosphate.^[31] Due to the high degree of condensation of $\kappa = 1$, N is four-fold coordinated, as well. Two different coordination environments appear: N1 is surrounded by three Be and one P atoms, whereas N2 is surrounded by two Be and two P atoms. The network topology can be described by the point symbol {3²⁴.4³³.5⁹}, which was determined with the TOPOS software. The point symbol matches that of analogous wurtzite.^[32]

Distances and angles in the tetrahedra (PN₄: 1.6624(2)–1.8536(4) Å; 103.394(4)–112.140(6)° and BeN₄: 1.7079(2)–1.7378(3) Å; 103.839(4)–111.497(6)°) are in the range with those in phe-BeP₂N₄ (PN₄: 1.622(3)–1.714(3) Å; 107.06(15)–112.95(14)°; BeN₄: 1.720(4)–1.754(4) Å; 106.7(2)–115.1(3)°) as well as in sp-BeP₂N₄ (BeN₄: 1.752(3) Å; 109.47(15)°).^[8-9]

Moreover, the Madelung Part of the Lattice Energy (MAPLE) of Be_2PN_3 was calculated to 116748 kJ mol⁻¹, which is in good agreement to the sum of the MAPLE values of formally constituting Be_3N_2 and P_3N_5 (118283 kJ mol⁻¹, 1.3% difference), and verifies the electrostatic consistency of the refined structure.^[33] CHARDI analysis underlines the structural model with an effective coordination number of 3.99 for Be and 3.72 for P and total charges of +2.01, +4.96 and -3.04 for Be, P and N, respectively (theory: Be: +2.0; P: +5.0; N: -3.00).^[34] More detailed information about the MAPLE and CHARDI calculations is provided in the Supporting Information.

To rule out incomplete condensation and the presence of imide groups which may form due to contact to air and moisture during the synthesis, Be_2PN_3 was analyzed by FTIR-spectroscopy (Figure S2.4). The FTIR spectrum shows no signal of N-H-valence modes but defined absorption bands below 1000 cm⁻¹, which can be assigned to vibrational (Be/P)N₄ modes of the Be-P-N network.

To verify the structural model, Be_2PN_3 was investigated by ⁹Be and ³¹P solid state MAS NMR spectroscopy. For the evaluation of the data for ⁹Be, quadrupolar interactions have to be taken into account ($I({}^{9}Be) = 3/2$) and hence, spectra were analyzed with the program DMFIT.^[35] The ${}^{9}Be$ spectrum (Figure 2.4) shows one narrow signal at 2.8 ppm (δ_{iso} = 4.0 ppm) corresponding to the one crystallographic Be site (8b). To the best of our knowledge, there exists no other NMR investigation of ⁹Be in a tetrahedral nitride coordination.^[36] Hence, we additionally determined the chemical shift of ⁹Be in α -Be₃N₂ with δ_{iso} = 5.3 ppm. The value for the chemical shift of Be₂PN₃ is in good agreement to the one of α -Be₃N₂. The NMR investigations combined with X-ray diffraction data and EDX measurements (Table S2.1) are sufficient to determine the structure built of BeN₄-tetrahedra and to exclude the presence of oxygen inside the sample: For BeN₄ tetrahedra, as found in α -Be₃N₂ or stated for Be₂PN₃, the quadrupolar interaction is small enough to result in the absence of the characteristic broadening of the central transition line shape (Be₃N₂: C_Q = 0.55 MHz, η_Q = 0.87; Be₂PN₃: $C_Q = 0.49$ MHz, $\eta_Q = 0.48$). For a theoretical BeN_{4-x}O_x (x = 1–3) tetrahedron, the quadrupolar interaction would increase due to the heterogeneous electronic environment. This would cause a significant broadening of the signal. For a BeO_4 tetrahedron, the quadrupolar interactions would again be small enough to result in a narrow signal, however shifted to δ_{iso} = 3.5 ppm, as for BeO $(C_Q = 0.45 \text{ MHz})$. In this case, the expected content of oxygen in EDX spectra would be much higher and the distance Be–X would be significantly shorter (Be–N: 1.7247(3) Å in Be₂PN₃, Be–O: 1.6458(8) in BeO^[37]).



Figure 2.4. ⁹Be MAS NMR spectrum of Be_2PN_3 showing one narrow signal at 2.8 ppm with experimental data (black) and fitting results for the central transition (red).

The ³¹P spectrum (Figure 2.5) shows one main signal at 43.4 ppm, which can be assigned to the one crystallographic P site (4*a*). The chemical shift is in the typical range of PN₄-tetrahedra as observed in other related compounds, for example Li₇PN₄.^[13] However, the shift differs from known nitridophosphates, for example MP_2N_4 (M = Sr, Mn, Cd) ($-27.7 < \delta_{iso} < 6.4$).^[10, 38] The explanation for this is provided by an examination of the second coordination sphere of phosphorus: While for MP_2N_4 (M = Sr, Mn, Cd) in the second coordination sphere other P atoms or even heavier atoms are present, for compounds like Be₂PN₃ or Li₇PN₄ only very light elements can be found. This lower electron density results in a greater unshielding of the P core and in a larger chemical shift. This phenomenon has also been investigated for lithium nitridophosphates.^[39] The broad minor signal at 49.4 ppm is most likely related to an amorphous side phase. All NMR spectra and experimental details are provided in the Supporting Information (Figure S2.6).



Figure 2.5. ³¹P MAS NMR spectrum showing one main signal at δ_{iso} = 43.4 ppm. The smaller broad signal at 49.4 ppm may arise from an amorphous side phase.

As for relatively mild reaction conditions (< 9 GPa) only BeP_2N_4 and Be_3N_2 were obtained, but no Be_2PN_3 , the thermal behavior of this compound was examined by temperature dependent powder X-ray diffraction under Ar atmosphere in the range from 50 to 900 °C (Figure S2.5). Be_2PN_3 is stable at ambient pressure until at least 900 °C. The thermal expansion of the material is quite small (average 6.5 ppm K⁻¹, Figure S2.6), indicating a very rigid network. Similarly small values for the thermal expansion have only been found in also highly condensed compounds like zeolites, other tectosilicates or phosphorus nitrides.^[40-42]

Since Be₂PN₃ is hard enough to scratch tungsten carbide, the elastic properties were examined by means of energy versus volume calculations (Figure S2.8) using the Vienna ab initio stimulation package (VASP).^[43-45] With a calculated bulk modulus $K_0 = 228$ GPa, Be₂PN₃ is as super-incompressible as α -Si₃N₄ (228 GPa).^[46] Based on the 6x6 elastic tensors derived from the first principles electronic structure calculations the Vickers Hardness H_v and the Fracture Toughness K_{lC} were determined to be approximately 29 GPa and 3.3 MPa m^{1/2}, respectively.^[47] Be₂PN₃ is a low-density hard material, harder than WC ($H_v = 27$ GPa, $K_{lC} = 7.5$ MPa m^{1/2})^[48-49] and in the range of OsB₂ ($H_v = 28$ GPa)^[50] or B₄C ($H_v = 30$ GPa, $K_{lC} = 3.1-3.7$ MPa m^{1/2})^[49, 51]. Furthermore, it is much harder and more incompressible than isostructural BeO ($B_0 = 212$ GPa; $H_v = 13$ GPa, $K_{lC} = 3$
3.7 MPa m^{1/2}).^[49, 52-53] The reason can be found in the high covalency of the Be-P-N network compared to the more ionic BeO. Due to its high hardness, the experimental determination of the optical properties of Be₂PN₃ was not possible. By grinding the sample in preparation for UV/VIS measurements, every grain gets coated with a thin layer of tungsten carbide. The so obtained darkish sample pretends metallic behavior in UV/VIS measurements. Hence, the optical properties were investigated with DFT calculations, alternatively. The average value for the band gap energy is with ~4.9 eV in good agreement within the expected range for a covalently bonded network. More information on the DFT calculations examining the optical and elastic properties is provided in the Supporting Information in Table S2.9 and S2.10.

Recently, we have reported on the synthesis and the properties of M_2PN_3 (M = Mg, Ca, Zn), raising the question of the existence of the lightest homologue.^[54-55] Starting from the binary nitrides Be₃N₂ and P₃N₅, Be₂PN₃ was synthesized under high-pressure and high-temperature conditions. The structure was elucidated by powder X-ray diffraction and confirmed by NMR spectroscopy, FTIR, EDX measurements as well as MAPLE and CHARDI calculations. The optical and elastic properties were examined by DFT calculations, indicating Be₂PN₃ as a hard, wide band gap material. High temperature powder X-ray diffraction reveals a very small shift in lattice parameters indicating a small thermal expansion and thus a rigid network. Considering the wide band gap and the thermal behavior, mixed phases with Mg₂PN₃, like Be_{2-x}Mg_xPN₃ (0 < x < 2), could be potential host materials for luminescent doping agents like Cr³⁺. Moreover, the synthesis of Be₂PN₃ demonstrates the combination of high-temperature-sensitive starting material like P₃N₅ gaining access to ternary beryllium nitrides with $\kappa = 1$. This approach may open access to other syntheses with temperature-unstable nitrides like Ge₃N₄.

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3. Synthesis and Comprehensive Studies of Be-IV-N₂ (IV = Si, Ge): Solving the Mystery of Wurtzite-Type *Pmc*2₁ Structures

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Abstract: The research for wurtzite-type ternary nitride semiconductors containing earth abundant elements with a stoichiometry of 1:1:2 was focused on metals like Mg or Zn, so far. The vast majority of these Grimm-Sommerfeld analogue compounds crystallize in the β -NaFeO₂ structure, although a second arrangement in space group Pmc2₁ is predicted to be a viable alternative. Despite extensive theoretical and experimental studies, this structure has so far remained undiscovered. Herein, we report on BeGeN₂ in a Pmc2₁ structure, synthesized from Be₃N₂ and Ge₃N₄ using a high-pressure high-temperature approach at 6 GPa and 800 °C. The compound was characterized by powder X-ray diffraction (PXRD), solid state nuclear magnetic resonance (NMR), Raman and energy dispersive X-ray (EDX) spectroscopy, temperature-dependent PXRD, second harmonic generation (SHG) and UV/VIS measurements and in addition also compared to its lighter homologue BeSiN₂ in all mentioned analytic techniques. The synthesis and investigation of both the first beryllium germanium nitride and the first ternary wurtzite-type nitride crystallizing in space group Pmc2₁ open the door to a new field of research on wurtzite-type related structures.

GaN and its doping varieties ($Al_xGa_vIn_{1-x-v}N$) show favorable properties for optoelectronic applications and can be found, for example, in LEDs, power electronics or solar cells.^[1-2] However, the availability of Ga and In is limited and the large lattice mismatch between GaN and InN limits the maximum In content to 20% before In segregation starts.^[3] Consequently, current research focuses on the synthesis and development of new wurtzite-type semiconducting nitrides based on earth abundant elements. According to the Grimm-Sommerfeld concept,[4-5] such nitride compounds can have the following stoichiometry: I-IV₂-N₃, II₂-V-N₃ (Na₂SiO₃-type)^[6-9], II-IV-N₂ $(\beta$ -NaFeO₂-type)^[6, 10-15] or II-VI-N₄ (enargite-type)^[16] with I = Li, Na; II = Zn, Mg, Mn; IV = Si, Ge; V = P; VI = Mo. Introducing O, even more structurally analogous compounds are possible like KGeON (LiSiON-type).^[17-18] All these examples can be derived from the initial wurtzite structure type. This relationship can be described via a Bärnighausen tree, which has already been formulated for this class of compounds in detail by Breternitz et al.^[19] Numerous such compounds combining different elements have been investigated in recent years and their properties have been intensively studied. Especially, semiconductors with earth abundant elements and stoichiometry 1:1:2 are interesting due to their similar band gaps and their improved tunability compared to $(Al_xGa_yIn_{1-x-y}N)$ like in (Mg,Zn)SnN₂.^[20-21] To the best of our knowledge, each of the wurtzite-type II-IV-N₂ Grimm-Sommerfeld analogous compounds crystallizes in the β -NaFeO₂ structure (space group *Pna*2₁) or a wurtzite structure with disordered cation positions, although three different other arrangements, represented by the space groups Pca2₁, Pmn2₁, and Pmc2₁ are theoretically possible.^[22-24] However, the arrangements in space groups $Pca2_1$ and $Pmn2_1$ break the octet rule of local charge neutrality and are therefore not favorable.^[23-24] In contrast, the octet rule obeying $Pmc2_1$ structure was predicted as a promising second candidate for II-IV-N₂ analogous compounds.^[25] Most recently, this modification was theoretically investigated for ZnSnN₂ with a calculated energy difference between the known β -NaFeO₂ and the *Pmc*2₁ structure of only 13 meV.^[26] Following, it was postulated that this small energy difference might be overcome during synthesis forming nanocrystalline regions of the Pmc2₁ structure, and Infrared and Raman spectra were theoretically calculated to analyze them.^[27] However, the synthesis of a wurtzite-type nitride crystallizing solely in space group Pmc2₁ was not successful, so far.^[19, 26] One condition for compounds to favor the Pmc2₁ structure, stated in the literature, is that the ions occupying the II and IV position should have a very similar ionic radius.^[19] A possible candidate for this requirement is BeSiN₂ (Be²⁺: 0.26 Å; Si⁴⁺: 0.27 Å).^[28] However, this compound crystallizes in the β -NaFeO₂ structure as well.^[10] Although the structure of BeSiN₂ is known since the 1960s, it was only part of several DFT studies but its optical properties have not been experimentally investigated, so far.^[29-33] While heavier homologues, like MgGeN₂, have already been synthesized, BeGeN₂ has only been studied theoretically.^[30, 32-34]

The reason might be that the synthesis of Be compounds is a challenge not only because of the toxic and harmful properties of the element Be, but also because of the difficult reaction conditions for activating the most commonly used starting material Be₃N₂. The synthesis of BeSiN₂, starting from the binary nitrides, is carried out at temperatures higher than 1800 °C.^[10] At this temperature, Ge₃N₄ would have already decomposed. To circumvent this problem, the high-pressure technique is a useful approach. Most recently we reported on the thermal activation of the refractory nitride Be₃N₂ and its reaction with thermally labile, but high-pressure stabilized P₃N₅ to synthesize highly condensed wurtzite-type Be₂PN₃.^[35] Consequently, we have adapted this method for the reaction of Be₃N₂ and Ge₃N₄.

In this contribution, we report on the discovery and bulk synthesis of $BeGeN_2$, which crystallizes in a unique structure. In addition, a comprehensive comparison to its lighter homologue $BeSiN_2$ is conducted. The title compound was synthesized using a high-pressure (HP) high-temperature (HT) approach at 6 GPa and 800 °C starting from Be_3N_2 and Ge_3N_4 according to Equation 3.1.

$$Be_3N_2 + Ge_3N_4 \rightarrow 3 \ BeGeN_2 \qquad (3.1)$$

The starting materials and 2% NH₄N₃ were thoroughly ground under Ar atmosphere, tightly packed into an *h*-BN crucible, then compressed and reacted in a large volume press obtaining a grayish powder. The color arises from small Ge impurities formed by the decomposition of small amounts of Ge₃N₄ at the reaction conditions. Consequently, the sample was washed with a 1:1 vol% mixture of concentrated NaOH with 30% H₂O₂ to remove Ge. The washed, colorless sample consists of crystals with a size up to 5 µm in length, as shown in Figure S3.1. EDX analysis detected no other elements than Ge, N and small amounts of O. Detailed information on the HP/HT synthesis of BeGeN₂ can be found in the Supporting Information.

For the comparison of the properties of $BeGeN_2$ with its lighter homologue, $BeSiN_2$ was synthesized according to Equation 3.2 by the reaction of Be_3N_2 and Si_3N_4 at 1900 °C in a radio-frequency furnace and was obtained in the form of plate-like crystals up to 40 µm length (Figure S3.1).^[10] More information on the synthesis of $BeSiN_2$ can be found in the Supporting Information.

$$Be_3N_2 + Si_3N_4 \rightarrow 3 BeSiN_2 \qquad (3.2)$$

Due to the small crystal size, the structure of BeGeN₂ was elucidated from powder X-ray diffraction (PXRD) data by using the Charge Flipping method and subsequent Rietveld refinement (*Pmc*2₁ (no. 26), a = 2.98324(5), b = 5.11633(8), c = 4.83927(8) Å, Z = 2, Figure S3.3, more details in the Supporting Information).^[36] As already shown, four different space groups are possible for the arrangement of the tetrahedra in a wurtzite-type II-IV-N₂ compound, namely *Pca*2₁, *Pma*2₁, *Pmn*2₁ and *Pmc*2₁ (see Figure S3.4). By comparing the theoretical diffraction patterns with the experimental one, it becomes clear, that BeGeN₂ crystallizes in space group *Pmc*2₁ (Figure 3.1).



Figure 3.1. Experimental powder diffraction pattern of BeGeN₂ (black) as well as the simulated diffraction patterns for all theoretically possible four space groups for BeGeN₂ derived from the wurtzite-type: $Pmc2_1$ (red), $Pna2_1$ (β -NaFeO₂-type, blue), $Pmn2_1$ (green) and $Pca2_1$ (orange).

During the refinement process no evidence for mixed occupancy was detected, ruling out a disordered wurtzite-type with statistical occupation of Be and Ge on the tetrahedra centers. The refined crystal structure and coordination polyhedra are illustrated in Figure 3.2 and 3.3. The structure consists of regular BeN₄ (green) and GeN₄ (brown) tetrahedra that are connected in all vertices. Due to the overall four-fold coordination of both Be and Ge, BeGeN₂ should be categorized as a double nitride rather than a beryllium nitridogermanate.^[37] Nitrogen is four-fold coordinated, too. Both N1 and N2 are surrounded by two Be and two Ge atoms. The network topology, determined with the TOPOS software, with the point symbol {3²⁴.4³³.5⁹} matches the one of analogous wurtzite.^[38]



Figure 3.2. The crystal structure of BeGeN₂ consists of all-side corner-sharing BeN₄ (green) and GeN₄ (brown) tetrahedra (N: blue). Viewed along [001] the wurtzite-type structure becomes apparent.



Figure 3.3. Coordination polyhedra of Be1 and Ge1.

Distances and angles of Be–N (1.73582(5)–1.77853(7) Å; 105.4172(13)–118.255(3)°) and Ge–N tetrahedra (1.86326(5)–1.91648(7) Å; 106.186(3)–111.7844(14)°) are consistent with those in phenakite-type BeP₂N₄ (Be–N: 1.720(4)–1.754(4) Å; 106.7(2)– 115.1(3)°)^[39], α -Be₃N₂ (Be–N: 1.731(11)–1.816(11) Å; 101.9(5)–120.9(5)°)^[40], and MgGeN₂ (Ge–N: 1.803(15)–2.089(15) Å; 104.3(6)–114.3(7)°).^[6]

The comparison of the structures of $BeSiN_2$ and $BeGeN_2$ raises the question of why $BeGeN_2$ crystallizes in space group $Pmc2_1$ and not $Pna2_1$. Considering the ratio of ionic radii it becomes clear, that $BeGeN_2$ comprises a unique combination of two cations, namely Be^{2+} (0.27 Å) and Ge^{4+} (0.39 Å) with a radius ratio of 0.69 (Table S3.7).^[28] More common combinations, e.g. $MgGeN_2$ or $ZnSnN_2$ show at least a ratio of 1. Hence, we assume that the ionic radius ratio of the cations and the corresponding volume of the tetrahedra are the reason for this unique structure type.

The calculation of the Madelung Part of the Lattice Energy (MAPLE) of BeGeN₂ (69999 kJ mol⁻¹) is in very good agreement with the sum of the MAPLE values of formally constituting Be_3N_2 and Ge_3N_4 (70244 kJ mol⁻¹, 0.4% difference).^[41] CHARDI analysis backs up the structural model with an effective coordination number of 3.97 for Be and 3.98 for Ge and average total charges of +2.00, +3.99 and -3.00 for Be, Ge and N, respectively. More detailed information for MAPLE and CHARDI calculations is provided in the Supporting Information.

To confirm the structural model and the presence of Be in the sample, ⁹Be MAS NMR experiments were performed with washed BeGeN₂. The ⁹Be spectrum (Figure 3.4) shows a single central-transition resonance around 4.7 ppm, compatible with one crystallographic site in BeGeN₂ (2*b*). For the evaluation of this signal, quadrupolar interactions have to be taken into account ($I(^9Be) = 3/2$). Analysis with the program DMFIT returns a quadrupolar coupling constant of $C_q = 0.49$ MHz and an isotropic chemical shift of $\delta_{iso} = 6.1$ ppm.^[42] The magnitude of C_q is thus in the range expected for a homonuclear, but slightly distorted tetrahedral coordination of the Be atoms.^[43] The value for δ_{iso} is in good agreement with Be₃N₂ ($\delta_{iso} = 5.3$ ppm)^[35] and BeSiN₂ ($\delta_{iso} = 5.5$ ppm, $C_q = 0.57$ MHz, Figure S3.5), which we determined in the same way. Hence, it can be assumed that the small oxygen content detected in the EDX spectra is likely to arise from surface hydrolysis. One reason might be the harsh washing conditions after the synthesis. More information on NMR measurements can be found in the Supporting Information.



Figure 3.4. ⁹Be MAS NMR spectrum of BeGeN₂ showing a single central-transition resonance around 4.7 ppm with experimental data (black) and fitting results (red).

Although the comparison of the diffraction pattern of BeGeN₂ with the theoretical ones (Figure 3.1) and the corresponding Rietveld refinement (Figure S3.3) is sufficient to determine the unique structure, we tested the hypothesis, that the β -NaFeO₂ modification can be distinguished from the structure in the *Pmc*2₁ space group solely on the basis of Raman spectroscopy.^[27] The differences in the spectra, displayed in Figure 3.5 become clearly apparent: For BeGeN₂ the experimental spectrum matches the calculated one for space group *Pmc*2₁ while the spectrum calculated for the *Pna*2₁ modification does not. For BeSiN₂ it is vice versa. Hence, the Raman spectrum confirms the presented structural model of BeGeN₂. Moreover, future identification of thin film BeGeN₂-type compounds could be feasible as stated by DFT calculations before.^[27]



Figure 3.5. Experimental Raman spectra (black) of BeGeN₂ (left) and BeSiN₂ (right) and the corresponding theoretical spectra for the space groups $Pna2_1$ (β -NaFeO₂-type) and $Pmc2_1$, respectively. In both cases, Raman data confirms the structural model found by XRD analysis. The differences of the spectra allow a differentiation between the two structure types by Raman data only.

Second harmonic generation (SHG) effects were examined for both compounds, confirming noncentrosymmetric space groups. The SHG signal for $BeGeN_2$ is comparable to the one of quartz (Table S3.11). More details on SHG measurements and calculations can be found in the Supporting Information.

DFT calculations for BeGeN₂ and BeSiN₂ in all four possible space groups show that the two space groups $Pmn2_1$ and $Pca2_1$ are less stable (Figure S3.6). This is to be expected, as the structures in these modifications do not obey the octet rule of local charge neutrality, as already discussed elsewhere.^[23-24] For BeGeN₂, the arrangement in $Pmc2_1$ is the most stable type with a difference of 18 meV (~1.7 kJ mol⁻¹) to the β -NaFeO₂-type ($Pna2_1$). For BeSiN₂ it is vice versa with a difference of 20 meV (~1.9 kJ mol⁻¹, Figure 3.6). The calculations are in line with our experimental results and in the same order of magnitude as DFT calculations on ZnSnN₂ disclosing a difference of 13 meV between the β -NaFeO₂ ground state and the crystal structure in space group $Pmc2_1$.^[26] More information on DFT calculations can be found in the Supporting Information.



Figure 3.6. Results of DFT calculations of BeSiN₂ and BeGeN₂ for possible wurtzite-type structures in $Pmc2_1$ and $Pna2_1$, confirming the experimental results.

The small energy differences between the different structure types arise the question, if phase transitions between them are possible. High-temperature PXRD for BeGeN₂ shows that the compound is stable up to 800 °C (Figure S3.7). Beyond this point it starts decomposing forming elemental Ge. BeSiN₂ stays stable at least until 900 °C (Figure S3.9) what is expected concerning the synthesis temperature of 1900 °C. According to the pressure-homologue rule, under pressure the lighter homologue should adopt the crystal structure of the heavier homologue.^[44] We intensively investigated the high-pressure behavior of BeSiN₂ in Diamond Anvil Cell (DAC) experiments until 90 GPa and up to 7800 K but could not observe any phase transition beside a small monoclinic distortion of the unit cell. However, the evaluation of experimental pressure-volume data reveals a bulk modulus K of 374(5) GPa (Figure 3.7, K' = 1.53(10)), which identifies BeSiN₂ as an ultra-incompressible material, far exceeding the calculated values of 220–263 GPa.^[29, 33, 45] More information on the DAC experiments and a discussion of the elastic properties of BeSiN₂ can be found in the Supporting Information.



Figure 3.7. Pressure-volume data from pressure-dependent single crystal refinements of $BeSiN_2$ were fitted with a 3rd order Birch-Murnaghan equation of state.

The optical properties of the two title compounds were examined by means of UV/VIS spectroscopy from diffuse reflectance spectra using the Kubelka-Munk function. (see Figure 3.8 and S3.13).^[46-47] The optical band gaps were determined to ~4.9 eV for BeGeN₂ and ~4.5 eV for BeSiN₂, assuming a direct band gap. The results are consistent with DFT calculations from the literature (Table S3.14). However, they are contrary to the trend of decreasing band gap energies towards the heavier homologue, as can be observed, for example, in Mg*M*N₂ (*M* = Si: 4.8 eV; Ge: 3.2 eV) or Zn*M*N₂ (*M* = Si: 3.7 eV; Ge: 3.2 eV).^[6, 11] More precise band gap measurement via X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) combined with DFT calculations could reveal whether this unusual difference in band gap energies arises from defects or whether it is influenced by the different arrangement of the tetrahedra, represented by different space groups, and will be part of future research.



Figure 3.8. Tauc plot for a sample of BeGeN₂ (black) with a tangent at the inflection point (red).

Recently, we have reported on the synthesis of II-IV-N₂ (II = Mg, Mn, Zn; IV = Si, Ge) and their solid solutions, raising the question of the existence of the light homologue $BeGeN_2$.^[6, 11, 48] Now, it was synthesized in a high-pressure high-temperature approach starting from the binary nitrides Be_3N_2

and Ge₃N₄. The compound crystallizes in a wurtzite-type structure in space group *Pmc*2₁, which has not been observed for any II-IV-N₂ compound so far. The structure was elucidated by PXRD, and confirmed by Raman and NMR spectroscopy as well as MAPLE, CHARDI and DFT calculations. SHG measurements confirm the non-centrosymmetric space groups for both compounds. While BeGeN₂ decomposes at temperatures higher than 800 °C, BeSiN₂, which was also investigated, shows neither a phase transition to the *Pmc*2₁ space group at higher temperature or higher pressure up to 90 GPa, nor any other phase transition, but an elastic module > 300 GPa was elucidated. Optical band gaps of both materials were measured with UV/VIS spectroscopy. Further studies on Be-IV-V₂ compounds (IV = Si, Ge; V = P, As, Sb) could shed light on whether the change in the structure type between the Si and Ge compound is a single event or whether it occurs systematically in Becontaining compounds with wurtzite-type structure.

Although, BeGeN₂ is the first wurtzite-type material crystallizing in the space group *Pmc*2₁ and more research will be needed to explore all properties of this new compound, a bulk usage of BeGeN₂ seems to be unfavorable due to serious safety concerns (see Supporting Information). However, the use of even small amounts of BeGeN₂ could give access to other II-IV-N₂ compounds in space group *Pmc*2₁: A thin film of just a few layers of BeGeN₂ could be grown, for example via chemical vapor deposition from BeCl₂ and GeCl₄ in NH₃ or suitable single crystals could be synthesized under ammonothermal conditions in an autoclave. The actual modification of this thin film can be assessed by Raman spectroscopy as we have demonstrated here for the bulk materials. On this layer of BeGeN₂, other compounds might be grown on epitaxially. Possible examples may be ZnGeN₂ or ZnSnN₂ via vapor-phase epitaxy out of volatile ZnCl₂, SnCl₄ in NH₃, via metalorganic precursors or molecular beam epitaxy.^[49-51] This synthesizing route could pave the way to the bulk synthesis of other BeGeN₂-type nitride semiconductors.

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4. Combination of Ambient and High-Temperature Beryllium Nitride Motifs in $W_2Be_4N_5$ and $W_4Be_8N_9$

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Abstract: Compounds of transition metals and beryllium have a wide range of applications, from everyday tools to high tech applications. Remarkably, no single ternary beryllium nitride with a transition metal is known. Here, we report on the synthesis and properties of the first transition metal nitridoberyllates, namely $W_2Be_4N_5$ and $W_4Be_8N_9$. Both compounds were synthesized in a hightemperature high-pressure approach from Be_3N_2 and W, using azide generated N_2 as an oxidizing agent. The crystal structures, consisting of alternating layers of WN_6 trigonal prisms and BeN_4 tetrahedra, were elucidated by single-crystal X-ray diffraction (sc-XRD). The separating nitridoberyllate layers show either ambient temperature (α -Be₃N₂ type) or high temperature (β -Be₃N₂ type) motifs. $W_2Be_4N_5$ was further corroborated by infrared (IR), nuclear magnetic resonance (NMR) and UV-VIS spectroscopy and vibrating sample magnetometry (VSM) measurements. The latter revealed a mixed valence with an intermediate oxidation state of 3.5 for the W atoms. Both, the synthesis of the first transition metal nitridoberyllates and the synthesis approach using elemental W pave the way to a new field of nitride chemistry.

Transition metal beryllium alloys are a well-studied class of materials with a wide range of applications. Remarkably, each transition metal, apart from the group 12 elements Zn, Cd and Hg, forms at least one intermetallic compound with Be.^[1-5] These materials are relevant for applications ranging from everyday life to high-tech applications: Beryllium bronzes are processed in non-magnetic and non-sparking tools, nickel beryllium alloys in Belleville springs in sprinkler heads or as contact springs in thermostats.^[6-7] Be₁₂Ti, on the other hand, is even envisaged as a neutron multiplier material in the blanket of fusion reactors and is supposed to be tested in ITER.^[8] In general, alloys containing Be are characterized by improved mechanical properties and higher temperature resistance.

Structurally different but similar in application is the compound class of transition metal nitrides. The use of TiN in drills or TaN during the chip production as barrier layer are examples of the high hardness and technical relevance of transition metal nitrides.^[9-10] Remarkably, new binary transition metal nitrides are still being discovered, most recently a high-pressure modification of W₂N₃ or W₃N₅, which exhibits superconducting properties.^[11]

Although, both classes of compounds exhibit exceptional properties such as high hardness or high electronic conductivity and both have practical applications, to the best of our knowledge there is no beryllium transition metal nitride, so far. The synthesis of such a compound promises to reveal new, previously unknown structural motifs and interesting properties. However, working with Be poses a number of challenges regarding reactivity of the Be precursors and safety precautions, which will be discussed in the following example: A first suggestion for the synthesis of a tungsten beryllium nitride could be the approach according to Rom et al., forming MgWN₂ in a tube furnace from Mg₃N₂ and W powder in a N₂ atmosphere.^[12] Such a reaction is unlikely for Be, since elemental tungsten is used as an inert crucible material for the synthesis of various beryllium nitrides, for example under high temperature conditions for $BeSiN_2$ or $SrBeSi_2N_4$ or even under increased pressure, as demonstrated for Sr₂BeAl₃N₅.^[13-15] Furthermore, the formation of a tungsten nitride only from W and N_2 without a sufficiently reactive nitride is unlikely, as tungsten is the standard crucible material in many nitride syntheses employing radiofrequency furnace setups.^[16] So the synthesis of multinary tungsten nitrides requires more reactive starting materials such as Mg₃N₂ or Ca_3N_2 . In contrast, Be_3N_2 is a relatively inert nitride used as a refractory. The second option, the use of a reactive tungsten species such as WCl₆ and a nitrogen source like azides, is not feasible for a beryllium compound as well: WCl₆ combined with, for example, NaN₃, is likely to produce an intermediate azide W(N₃)₆ in a metathesis reaction,^[17] which is very sensitive and can accidentally detonate. This would produce finely dispersed dust of Be₃N₂, which must be avoided in any case. A third option could be application of a sputtering technique, as shown on the example of Mg₃WN₄. However, related experiments have resulted in the formation of α -Be₃N₂ and W₂N and not a ternary compound.^[18]

Faced with all these synthetic challenges, we have combined our approach of high-temperature and high-pressure activation of Be_3N_2 , as demonstrated on the example of Be_2PN_3 , with the method of *Kloß et al.* of oxidizing transition metals under high pressure conditions by in situ generated, elemental N_2 , as described on the example of Ca_4FeN_4 .^[19-20]

Here, we report on the synthesis of the first transition metal nitridoberyllates, $W_2Be_4N_5$ and $W_4Be_8N_9$, and their challenging structure elucidation. $W_2Be_4N_5$ was synthesized in a high-temperature (HT) high-pressure (HP) approach at 8 GPa and 1350 °C from Be_3N_2 , elemental W and NH_4N_3 or NaN_3 according to Equations 4.1 and 4.2.

$$4 \text{ Be}_{3}\text{N}_{2} + 6 \text{ W} + 3 \text{ NH}_{4}\text{N}_{3} \rightarrow 3 \text{ W}_{2}\text{Be}_{4}\text{N}_{5} + 4 \text{ NH}_{3} + \frac{1}{2} \text{ N}_{2} \quad (4.1)$$

$$4 \text{ Be}_{3}\text{N}_{2} + 6 \text{ W} + 3 \text{ NaN}_{3} \rightarrow 3 \text{ W}_{2}\text{Be}_{4}\text{N}_{5} + 3 \text{ Na} + \text{N}_{2}$$
(4.2)

The starting materials were finely ground in a glovebox under Ar atmosphere, packed into an *h*-BN crucible and compressed and reacted in a large volume press obtaining a dark-red powder. Using NaN₃ as a nitrogen source, the product was additionally washed with water to remove elemental Na. W₂Be₄N₅ crystallizes as red, plate-like crystals with a diameter up to 10 μ m and a thickness up to 650 nm (Figure 4.1 and S4.1), which are stable to air, water, dilute NaOH and HCl as well as oxidizing agents like 10% H₂O₂. EDX analysis revealed no other elements than W, N and small amounts of O. Beryllium cannot be detected with EDX spectroscopy next to W. W₄Be₈N₉ was serendipitously discovered during an attempt to grow larger crystals of W₂Be₄N₅ by prolonged dwelling at the synthesis temperature. Detailed information on the HT/HP synthesis of W₂Be₄N₅ and W₄Be₈N₉ can be found in the Supporting Information.



Figure 4.1. Exemplary SEM image of crystals of $W_2Be_4N_5$. Crystals are up to 10 μm in diameter and 650 nm thick.

The structure of $W_2Be_4N_5$ was elucidated by the combination of several analytic techniques. Singlecrystal X-ray diffraction (sc-XRD) revealed rhombohedral metrics (a = 2.86870(10), c = 37.0749(13) Å) and the arrangement of WN_6 trigonal prisms (gray) in space group $R\overline{3}m$ (no. 166, see Figure 4.2). This arrangement of trigonal prisms is analogous to that in NbSe₂ upon doping with Rb.^[21] The crystals show an obverse/reverse twinning. A detailed guide on how to proceed with this type of twinning can be found in the literature.^[22]



Figure 4.2. The crystal structure of $W_2Be_4N_5$ (left, along [110]) consists of layers of WN₆ trigonal prisms, that are separated by layers of edge-sharing BeN₄ tetrahedra (middle). Viewed along [1 2 10] the different connectivity of the Be–N layers become apparent (right). W: gray; Be: green, N: blue.

Filling the space between the layers of WN₆ prisms, results in two competing structural models. One model, with reduced symmetry, in space group R3m with corner sharing BeN₄ tetrahedra and one that remains in space group R_3^{3m} with edge sharing BeN₄ (see Figure S4.2). Both models are reasonable from a chemical point of view, since corner sharing BeN4 tetrahedra are a well-known structural motif, for example in BeSiN₂ or Be₂PN₃,^[13, 19] while edge sharing BeN₄ occur in α -Be₃N₂, $AEBe_{20}N_{14}$ (AE = Sr, Ba) or MgBe₂N₂.^[23-25] Both structural models show similar quality parameters due to the very weak scattering contribution of the Be atoms, but the centrosymmetric model is slightly better and allows for anisotropic refinement of the N atoms. SHG measurements to elucidate a non-linear behavior were not possible due to the strong absorption of the sample in the visible. However, the sum formula of the two models and thus the atomic ratio of Be:W is different (R3m: W₂Be₃N₅ with W:Be of 2:3; $R\overline{3}m$: W₂Be₄N₅ with W:Be of 1:2). Measurements on washed samples using inductively coupled plasma optical emission spectrometry (ICP-OES) revealed a W:Be ratio of 1:1.9, which is consistent with the centrosymmetric model. Based on the results of the elemental analysis and the better quality factors with simultaneously less refined parameter in the sc-XRD refinement, we decided to favor the model of $W_2Be_4N_5$ in space group R_3m as depicted in Figure 4.2.^[26]

The layers of trigonal prisms of WN₆ are separated by layers of edge sharing BeN₄ tetrahedra. The closer spacings contain BeN₄ tetrahedra as they occur in the ambient temperature polymorph α -Be₃N₂.^[27] The wider spacings are also filled with edge-sharing BeN₄ tetrahedra, but in a conformation as found in the high-temperature form β -Be₃N₂.^[28] The occurrence of ambient and high-temperature beryllium nitride motifs is so far uncommon and could be the result of the combination of high-temperature and high-pressure synthesis conditions. Combining a tungsten layer with its next neighbored Be-N layer to form a sublayer, results in a stacking order of aba'b'a''b'' or ABC. The refined crystal structure and coordination polyhedral are illustrated in Figure 4.2 and 4.3. The network topology was determined with the TOPOS software to {3¹⁵.4¹⁸.5³} for the α -Be₃N₂ type layer and {3³³.4³³} for the β -Be₃N₂. To the best of our knowledge, this topology has not yet been found in one single compound, but is however related to those of α - and β -Be₃N₂ (α : {3⁴⁷.4⁶⁸.5⁵}; β : {3²⁷.4³⁶.5³}{3⁴⁵.4⁶⁰.5¹⁵}²}). With respect to the four-fould coordination of Be and the formation of an anionic network, W₂Be₄N₅ should be categorized as a tungsten nitridoberyllate.^[29] Further information on the refinement of the crystal structure is given in the Supporting Information.



Figure 4.3. Coordination polyhedra of W1, Be1 and Be2 in W₂Be₄N₅. The thermal ellipsoids are shown at 90% probability level. For the Be atoms, anisotropic values could not be determined.

Distances and angles of WN₆ trigonal prisms (2.097(7)–2.111(7) Å) and BeN₄ tetrahedra, forming the β -Be₃N₂ type layers (Be2; 1.66(4)–1.802(14) Å; 105.5(11)–113.2(10)°) are consistent with those in h-W₂N₃ (2.1626(14) Å) or FeWN₂ (2.155(5) Å)^[30-31] and in β -Be₃N₂ (1.70(2)–1.794(8) Å; 104.7(7)–113.9(6)°).^[32] The individual distances in the BeN₄ tetrahedra (Be1; 1.53(3)–1.880(14) Å), which form the α -Be₃N₂ type layer, differ from the usual distances (α -Be₃N₂: 1.724–1.816 Å), but the average bond length of 1.7925 Å is in line with that from the binary nitride (α -Be₃N₂: 1.7533 Å).^[23] One possible reason for this observation could be that the equilibrium position of Be1 next to the W atoms cannot be perfectly refined due to termination effects of the tungsten atoms. Another reason could be that the Be atoms only fill available gaps left in the structure, mainly defined by the tungsten nitride layers. X-ray diffraction data at high angles, collected for example at a synchrotron, could reveal deeper insight and will be part of future research.

CHARDI analysis supports the structural model with an effective coordination number of 3.77 for Be and 5.99 for W and average total charges of +2.01, +3.55 and -3.02 for Be, W and N, respectively.

Magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy of washed samples of $W_2Be_4N_5$ confirms the presence of Be inside the sample (Figure S4.5).

The combination of the structural model obtained from sc-XRD with the PXRD data by a Rietveld refinement, reveals the high phase fraction of the presented synthesis route (Figure S4.3).

As mentioned above, $W_4Be_8N_9$ was obtained by the attempt to grow larger crystals of $W_2Be_4N_5$ by longer dwelling at the synthesis temperature and a longer cooling ramp. $W_4Be_8N_9$ crystallizes in plate-like crystals of similar size to those of $W_2Be_4N_5$ but with a metallic black color. The structure was elucidated by sc-XRD ($R\overline{3}m$; a = 2.8647(3); c = 67.273(7) Å, Z = 3, Table S4.5) based on the model of $W_2Be_4N_5$.^[26] For the sake of better visualization, the structure is displayed in the Supporting Information due to the long *c*-axis (Figure S4.7). $W_4Be_8N_9$ is a stacking variant of $W_2Be_4N_5$ which can also be described by the stacking order aba'b'a''b'' or ABC. However, the "a" sublayers of $W_4Be_8N_9$ consist of three "a" layers of $W_2Be_4N_5$, while the "b" sublayers are identical. The distances and angles of BeN₄ and WN₆ polyhedral agree with the results for $W_2Be_4N_5$. A phase pure synthesis of $W_4Be_8N_9$ was not feasible, but $W_2Be_4N_5$ is the only side phase as identified by Rietveld refinement (Figure S4.4). Further annealing (> 120 min) at synthesis conditions did not lead to an increase in the phase fraction, but to decomposition into WN and other unidentified, poorly crystalline products. However, further stacking variants seem to be likely. More information on $W_4Be_8N_9$ can be found in the Supporting Information.

The formation of W₄Be₈N₉ for longer dwelling times raises the question of whether the two phases can be converted into each other. High-temperature PXRD (HT-PXRD) shows the stability of W₂Be₄N₅ at least up to 800 °C (Figure S4.8). The thermal expansion of the material is quite small (α_a = 6.3(2); α_c = 9.6(7) ppm K⁻¹) and in the same order of magnitude as that of sapphire, indicating a rigid network.^[33] A conversion of W₂Be₄N₅ into W₄Be₈N₉ or vice versa was not observed (Figure S4.10).

The bulk material of $W_2Be_4N_5$ shows a black to dark-red color with strong reflectance of the agglomerates. However, when these agglomerates are broken up, the individual crystals (thickness: approx. 600 nm) show a deep-red color under intense light (Figure S4.1). The same applies to the powder. Therefore, the optical properties of $W_2Be_4N_5$ were examined by UV-VIS spectroscopy from diffuse reflectance spectra using the Kubelka-Munk function. The optical band gap was determined to ~1.8 eV (~690 nm), which is consistent with the visual impression of the red crystals (Figure 4.4).



Figure 4.4. Tauc plot for a sample of $W_2Be_4N_5$ (black) with a tangent at the inflection point (red). The value of ~ 1.8 eV is consistent with the color impression of the crystals (inset).

The sum formula $W_2Be_4N_5$ raises the question of the oxidation state of the W atoms. The sum formula gives a formal charge of +3.5 for each tungsten atom, what is in line with the CHARDI calculations (see above), however lower compared to other compounds containing [WN₂] layers, e.g. LiWN₂. This type of materials is synthesized by ammonolysis of a W(VI) compound like Li₂WO₄.^[34] W₂Be₄N₅, on the other hand, is synthesized from elemental W, which is oxidized by *in situ* generated N₂. The chemical potential of N₂ is increased under synthesis conditions, but might be still too low for a higher oxidation state of the tungsten atoms in the found compound.^[35]

The magnetic properties were examined using a vibrating sample magnetometer. The isothermal magnetization corresponds to a diamagnetic behavior with a small ferromagnetic offset (Figure 4.5, 0.08 G at H=0), which arises from ferromagnetic impurities, e.g. the use of iron spatulas or the contamination of the W powder with ferromagnetic elements like Fe or Co. The diamagnetic behavior of the sample indicates an intermediate occupation of the tungsten site. This means that the electron responsible for the +III or +IV oxidation state is delocalized inside the tungsten layers and thus, no particular W³⁺ or W⁴⁺ sites are present. This is consistent with the crystallographic model, which has only one tungsten site. For distinct oxidation states we would expect two different sites with different polyhedral volumes. To verify our results, we also investigated the magnetic properties of a related compound, namely h-W₂N₃ that was synthesized according to Wang et al.^[30] Only one tungsten site is described in the structural model and a formal charge of +4.5 can be derived from the sum formula. The tungsten atoms are coordinated by nitrogen in trigonal prisms as in $W_2Be_4N_5$. The thermal magnetization for W_2N_3 also shows a diamagnetic behavior with a ferromagnetic offset (Figure S4.12). The susceptibility plots for all samples show a very weak paramagnetic behavior due to the paramagnetic impurities (Figure S4.11 and S4.12). Further information on the magnetic properties can be found in the Supporting information.

At this point it is worth mentioning that we have considered the presence of oxygen or imide groups within the structure. A theoretical $W_2Be_4N_4O$ or $W_2Be_4N_4NH$ would exhibit two W^{3+} . However, we are confident that there is no O or N-H present in the sample for the following reasons: To exclude NH₃ during the reaction, the synthesis was repeated using NaN₃ as the nitrogen source (Equation 4.2). $W_2Be_4N_5$ as well as elemental Na were obtained. The infrared (IR) spectroscopy measurements

of different samples show no characteristic signals of N-H valence modes (Figure S4.6). At the same time, the presence of elemental Na is a strong indicator, of the absence of oxygen, since the formation of Na₂O or even Na₂O₂ could not be observed. Finally, we have tried to reproduce our result presenting O during the reaction in form of oxygen-containing starting materials like BeO, and have not obtained W₂Be₄N₅, but poorly crystalline samples. However, the unambiguous exclusion of oxygen in the structure of W₂Be₄N₅ can only be achieved by neutron diffraction due to the different scattering lengths of N and O.



Figure 4.5. Isothermal magnetization at 2 and 300 K for a sample of W₂Be₄N₅. It shows a diamagnetic behavior with a ferromagnetic offset.

Most recently, *Rom et al.* reported on the synthesis of MgWN₂ and Mg₃WN₄, raising the question of the existence of a beryllium tungsten nitride.^[12] Now, two new materials, namely W₂Be₄N₅ and W₄Be₈N₉ have been synthesized in a high-pressure high-temperature approach by the reaction of Be₃N₂ with elemental W and NH₄N₃ or NaN₃. Both compounds crystallize in plate-like crystals in space group $R\bar{3}m$. The structure of W₂Be₄N₅ was elucidated by a combined approach of single-crystal X-ray diffraction, elemental analysis, IR measurements as well as CHARDI calculations. It consists of layers of WN₆ trigonal prims that are separated by edge-sharing BeN₄ tetrahedra, which show either ambient or high-temperature motifs of the binary nitride Be₃N₂. While the bulk material exhibits a black or dark-red color, single crystals of W₂Be₄N₅ with a thickness of 600 nm show a red color. VSM measurements reveal a diamagnetic behavior of W₂Be₄N₅ and thus suggests an intermediate ordering of the W atoms. W₄Be₃N₉ crystallizes in a stacking variant of W₂Be₄N₅ and is formed by longer dwelling times at synthesis conditions. Both compounds are stable up to at least 750 °C and cannot be converted into each other.

The synthesis route presented here paves the way to further transition metal beryllium nitrides, which are expected to yield not only a variety of structures, but also outstanding properties for a wide range of potential applications, keeping in mind transition metal beryllium alloys. The main advantage of the synthesis route is the avoidance of reactive WCl₆ and the activation of the refractory material Be₃N₂ at the same time. It also has been shown that bulk synthesis is feasible, which could be applied to Mg₃WN₄, of which only thin films could be produced so far.^[12] A comparison of the structures of MgWN₂ and W₂Be₄N₅, shows that W is coordinated in a trigonal prism in both compounds. However, the group II cation in $W_2Be_4N_5$ is coordinated in BeN₄

tetrahedra, whereas in MgWN₂ it is coordinated in MgN₆ octahedra. High-pressure experiments, for example in a diamond anvil cell, could show whether Be can change its coordination number to six in a ternary nitride and elucidate the mechanical properties of the new compounds. So far, the only known material with BeN₆ octahedra is BeN₄, which was synthesized at 80 GPa.^[36]

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5. High-Pressure Synthesis of Ultra-Incompressible Beryllium Tungsten Nitride Pernitride BeW₁₀N₁₄(N₂)

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Abstract. For the activation of nitrogen and its reduction to ammonia, transition metals are crucial in biological as well as industrial processes. So far, only a few binary transition metal compounds with nitrogen dimer anions are known, while a ternary compound has remained undiscovered as yet. Here, we report on the synthesis and properties of the first ternary transition metal compound, namely $BeW_{10}N_{14}(N_2)$, which exhibits dinitrogen anions. It was synthesized in a high-temperature high-pressure approach from $W_2Be_4N_5$. The crystal structure, elucidated with synchrotron radiation, unites WN_7 capped trigonal prisms with intriguing BeN_6 octahedra and (N_2) -anions. Elastic and electronic properties of the title compound were corroborated by DFT calculations, revealing simultaneous ultra-incompressible and metallic behavior. The synthesis and investigation of the first ternary transition metal nitride with dinitrogen units opens the door to a new field of research on nitride and pernitride chemistry.

Transition metal catalysts are essential for the activation of nitrogen and its reduction to ammonia. Examples include the well-known Haber-Bosch process, which uses an iron-based catalyst, and the enzyme nitrogenase, which contains a Fe-Mo-cofactor.^[1-4] In the Yandulov-Schrock cycle, a Mobased catalyst enables the reduction of the N₂ molecule in the only artificial process at ambient conditions.^[5-7] The reduction can be followed via several stages represented by the oxidation states of the nitrogen dimer of 0, -II or -IV. The corresponding molecules/anions would be dinitrogen, diazenide or hydrazide anions. The latter is isoelectronic to the peroxide ion O_2^{2-} and hence can be named analogously as pernitride. Many inorganic compounds are known to stabilize these intermediate dinitrogen units, for example AEN_2 (AE = Ca, Sr, Ba)^[8-9] for the diazenide (N_2)²⁻ ion or OsN_2 , IrN_2 , PtN_2 or TiN_2 for the pernitride anion $(N_2)^{4-}$.^[10-12] However, recent discoveries show that formal charges of -1 or -3 are also possible for the N₂ unit as found in LiN₂ or FeN₂, respectively.^{[13-} ^{15]} Furthermore, nitrogen dimers with non-integer charges were found in $M_3(N_2)_4$ (M = Na, Ca, Sr, Ba).^[16-17] The "inert" element nitrogen becomes highly reactive under suitable conditions, creating unprecedented structures and polyhedra that have not been previously observed in nitrides;^[18] for example BeN₆ octahedra in the polynitride BeN₄, synthesized at 84 GPa.^[19] While tremendous efforts in the research of binary nitrides, diazenides, pernitrides and polynitrides have expanded our knowledge in this field, we hardly know anything about ternary compounds with $(N_2)^{x-1}$ anions. The only exception is $Li_2Ca_3(N_2)_3$,^[20] which, to the best of our knowledge, is the only ternary compound with dinitrogen units, known until now.

Recently, we have reported the synthesis of the first transition metal nitridoberyllates $W_2Be_4N_5$ and $W_4Be_8N_9$.^[21] We raised the question whether the formation of BeN₆ octahedra is possible in a high-pressure modification of $W_2Be_4N_5$ according to the pressure homologue rule in analogy to the structurally related MgWN₂.^[22-23] Driven by this question, we have probed the high-pressure behavior of $W_2Be_4N_5$. Upon heating of $W_2Be_4N_5$ at elevated pressure, we discovered BeW₁₀N₁₄(N₂), which not only exhibits BeN₆ octahedra but is also the first ternary transition metal compound to contain dinitrogen anions. The title compound may be seen as the first ternary nitride pernitride as this combination of nitride and dinitrogen anions is so far only known in binary compounds, e.g. in SrN (Sr₈N₄(N₂)₂), Re(N₂)N₂ or Mo₃(N₂)N₃.^[24-26] Li₂Ca₃(N₂)₃ exhibits solely dinitrogen anions and no nitride ions.^[20]

The starting material $W_2Be_4N_5$ was synthesized according to Equation 5.1 in a large volume press at 8 GPa and 1400 °C.

$$4 \text{ Be}_{3}\text{N}_{2} + 6 \text{ W} + 3 \text{ NaN}_{3} \rightarrow 3 \text{ W}_{2}\text{Be}_{4}\text{N}_{5} + 3 \text{ Na} + \text{N}_{2}$$
(5.1)

In order to confirm the structural model of W₂Be₄N₅ and to identify a suitable crystal for the diamond anvil cell (DAC) experiment, single crystal X-ray diffraction (sc-XRD) data were collected at ambient pressure. The integration of diffraction data collected from a strongly scattering domain yielded an appropriate data set, from which the structure of W₂Be₄N₅ was determined (*a* = 2.8702(2), *c* = 37.1324(18) Å; $R\bar{3}m$ (no. 166), R_1 = 0.0254).^[27] The structure obtained here validates the model which we have reported before and clarifies structural details (Figure S5.1).^[21] More information on the synthesis and the refined crystal structure of W₂Be₄N₅ can be found in the Supporting Information.

To investigate the elastic properties of $W_2Be_4N_5$, a DAC was loaded with a single crystal and Ne as pressure transmitting medium. The sample was compressed at ambient temperature in seven steps up to a pressure of 41.0(1) GPa. At each step, sc-XRD data was collected to elucidate the pressure-dependence of the lattice parameters and unit cell volume (Figure 5.1 and S5.2). The unit cell volume decreases by approximately 11% over the examined pressure range. The pressure-volume data were fitted with a second-order Birch-Murnaghan equation of state revealing an isothermal bulk modulus $K_0 = 273.4(2)$ GPa with a fixed value for K' = 4.00 (Figure 1).^[28] The lattice parameters *a* and *c* show a similar compressibility up to approximately 27 GPa (Figure S5.2). Beyond this pressure point, the *c*-axis is more compressible. The evaluation of the sc-XRD data revealed no pressure-induced phase transition on compression at ambient temperature. More information on the elastic properties and the DAC setup can be found in the Supporting Information.



Figure 5.1. Pressure-volume data from pressure-dependent single crystal refinements of $W_2Be_4N_5$ were fitted with a 2nd order Birch-Murnaghan equation of state.

To induce a phase transition or reaction, the single crystal was laser heated from both sides at 41.0(1) GPa (NIR fiber laser, $\lambda = 1064$ nm) for approximately 30 seconds. The temperature was likely above 3000 K based on previous observations, but was not precisely determined. The pressure was determined after the heating to 42.1(1) GPa. The subsequent XRD scan showed a clearly altered diffraction pattern and the formation of different crystalline phases. One of the new phases was the

high-pressure modification of the binary nitride W_2N_3 (a = 7.712(7), b = 2.7953(5), c = 8.059(2) Å; *Pnma* (no. 62)), which we have already reported on elsewhere.^[29] From the analysis of another dataset, we determined the structure of the first ternary transition metal pernitride BeW₁₀N₁₄(N₂). Its structure was solved and refined in space group *C*2/*m* (no. 12) with a = 19.803(5), b = 2.7867(6), c = 8.2467(15) Å, $\beta = 99.605(19)^\circ$ and Z = 2 at 42.1(1) GPa.^[27]

The refined crystal structure and coordination polyhedra are illustrated in Figure 5.2. The structure consists of WN₇ single-capped trigonal prims, regular WN₆ trigonal prisms, BeN₆ octahedra and (N₂)-units. The W–N polyhedra are interconnected by vertex-, edge- and surface-sharing. This structural motif is known from other tungsten nitrides like W₂N₃ or W₃N₅.^[29] A special feature is the connection of several WN₇ capped trigonal prims via the (N₂) unit, so far only known from W₃N₅. The voids in the basic structure formed from tungsten and nitrogen are filled with Be atoms forming edge-sharing BeN₆ octahedra that are stacked along the *b*-axis. This structural motif has not yet been observed in a nitride compound. The only other phase with BeN₆ octahedra is BeN₄, whereas in its structure the BeN₆ octahedra are connected via pernitride units.^[19]

It is remarkable that Be in sixfold coordination can be obtained at the relatively low pressure point of 42.1(1) GPa in a nitride. In comparison, BeN₄ was synthesized at 84 GPa and undergoes a phase transition when pressure is reduced. The formation of BeO₆ octahedra is known from a high-pressure polymorph of the mineral hurlbutite, CaBe₂(PO₄)₂, when compressed above 90 GPa.^[30] However, *Spahr et al.* demonstrated that in calcite-type BeCO₃ Be in sixfold coordination can be formed already at a pressure of approx. 30 GPa.^[31] Moreover, *Pointner et al.* synthesized P_{1-x}Ta_{8+x}N₁₃ (x = 0.1-0.15), which exhibits the common high-pressure motif of PN₆ octahedra, previously synthesized at approx. 40 GPa (spinel-type BeP₂N₄ or β -BP₃N₆) at only 8 GPa in a large volume press.^[32] Considering these recent discoveries, the presence of BeN₆ octahedra at a pressure of approx. 40 GPa seems plausible.



Figure 5.2. Crystal structure (a,b) and coordination polyhedra of cations of $BeW_{10}N_{14}(N_2)$ (c) at 16.5(1) GPa. The structure consists of WN_7 single capped trigonal prisms, regular WN_6 trigonal prims and BeN_6 octahedra. Viewed along the *c* axis, the stacking of the octahedra along *b* via edge sharing becomes apparent (b). Be: green, W: gray, N: blue. The (N₂)-dumbbell is cyan colored.

The distances in the W–N polyhedra (1.96(4)–2.23(5) Å) are consistent with those in W₂N₃ (2.02(3)–2.115(19) Å) and W₃N₅ (1.954(11)–2.106(5) Å).^[29] The interatomic distances for BeN₆ octahedra (1.78(6)–2.06(3) Å) can only be compared to those of BeN₄ measured at 84 GPa (1.667(4)–1.827(3) Å) and therefore only allow to state that these distances are similar.^[19] The (N₂) unit has a bond distance of 1.35(12) Å, in reasonable agreement with distances in FeN₂ (1.307(10)),^[14-15] or RhN₂ (1.30(5)).^[33-34] Since no framework with a negative charge built up from BeN₄ tetrahedra is present, and with respect to the formula BeW₁₀N₁₄(N₂), the new compound should be classified as a beryllium tungsten nitride pernitride rather than a tungsten nitridoberyllate, as is appropriate for W₂Be₄N₅.^[35] More detailed information on the crystal structure of BeW₁₀N₁₄(N₂) at different pressure points, reconstructed *hkl* planes and a Le Bail fit can be found in the Supporting Information.

The weak atomic form factor of Be adjacent to the strongly scattering W and the low completeness of the data set, which is due to the measurement of a monoclinic system in a DAC, raises the question of whether the position of Be atoms can be determined accurately.^[36-37] However, the refinement of alternative structural models gave unsatisfactory results and were abandoned, but from the experimental data we cannot rule out disorder within the channels.

In order to independently confirm the structural model derived from experiment, DFT-based model calculations were carried out. The full geometry optimizations yielded a relaxed structure in very good agreement with the structural model derived from experiment (see Table S5.5–S5.11 and S5.13–S5.17). Based on this agreement, we computed the enthalpy change due to the incorporation of Be into a theoretical $W_{10}N_{16}$, according to Equation 5.2.

$$Be + W_{10}N_{16} \to BeW_{10}N_{16}$$
 (5.2)

The incorporation of beryllium according to Equation 5.2, is highly preferred with $\Delta H = -5.348 \text{ eV}$ per unit cell, i.e. 256 kJ/mol.

Additionally, we have explored if small atoms such as Ne, which was employed as a pressuretransmitting medium, would be incorporated into the channels. However, the analysis of the sc-XRD data provided no indication of such an incorporation and the corresponding DFT calculations implied that in the athermal limit such an incorporation would be energetically unfavorable.

Furthermore, the DFT calculations also strengthened the arguments for the presence of a (N₂) dimer. The computed N-N distance at 40 GPa in the dimer is d(N-N) = 1.388 A, in good agreement with the experimental value (1.35(12) Å). The N-N bond has a Mulliken population of 0.65 e-/A**3, i.e. this is a predominantly covalent bond.

In order to answer the question if $BeW_{10}N_{14}(N_2)$ is stable at ambient pressure, the sample was decompressed. While the crystal quality of $BeW_{10}N_{14}(N_2)$ degrades with decreasing pressure, we could still observe the phase at ambient pressure. Unfortunately, sc-XRD data could only be collected at two pressure points during decompression. Hence, the decompression data was complemented with data from the DFT calculations. Figure 5.3 shows the experimental and theoretical data. The analysis of the DFT compression data gave a bulk modulus of $K_0 = 338.5(4)$ GPa with a pressure derivative of K' = 4.61(3). The experimentally determined unit cell volumes are

systematically smaller than those obtained from the DFT calculations. This is due to the underbonding typically encountered in DFT-GGA-PBE calculations such as those which have been carried out here. Bulk moduli of DFT-GGA-PBE are typically lower than the corresponding experimental values.^[38-39] The evaluation of the elastic stiffness tensor from stress-strain DFT calculations with the program ELATE revealed an isothermal bulk modulus $K_0 = 337$ GPa, in very good agreement with the value obtained from the equation of state. Accordingly, BeW₁₀N₁₄(N₂) can be described as an ultra-incompressible material, as it has a bulk modulus > 300 GPa.^[40-41] However, high incompressibility does not necessarily correlate with high hardness, which is reflected by the value of the Vickers hardness H_v of approximately 21 GPa derived from the elastic stiffness tensor.^[42] The examination of the electronic properties of BeW₁₀N₁₄(N₂) using DFT calculations revealed metallic behavior (Figure S5.7), in line with the results of the only other ternary pernitride Li₂Ca₃(N₂)₃. More information on DFT calculations, the elastic and electronic properties can be found in the Supporting Information.



Figure 5.3. Pressure-volume data for $BeW_{10}N_{14}(N_2)$ from DFT calculations fitted with a 3rd order Birch-Murnaghan equation of state. Error bars associated with the experimental data are smaller than the symbol size.

In summary, we have synthesized the first ternary transition metal pernitride $BeW_{10}N_{14}(N_2)$ at 42 GPa, which also exhibits BeN_6 octahedra at far lower synthesis conditions than before (84 GPa for BeN_4).^[19] The crystal structure was elucidated in a combined approach from sc-XRD synchrotron data and DFT calculations. The structure exhibits anions of (N₂) dimer units that were not observed in a ternary transition metal compound, so far. The examination of combined experimental and theoretical pressure-volume data revealed ultra-incompressible behavior with a bulk modulus $K_0 = 337$ GPa. Additionally, the compound is quenchable to ambient pressure. The calculation of the electronic structure reveals metallic properties.

The synthesis of $BeW_{10}N_{14}(N_2)$ lays the foundation for the synthesis of further ternary transition metal pernitrides. Due to the structural relationship of Be and Fe in high-pressure synthesized compounds like BeN_4 and FeN_4 , the possibility of the synthesis of a ternary iron-tungsten pernitride seems likely.^[14, 19] This model compound could shed light on the nitrogen fixation process and its intermediate steps occurring in the Fe-Mo-cofactor in the natural enzyme nitrogenase.^[3-4]

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6. Summary

The scope of this thesis was to overcome barriers in the synthesis of beryllium nitrides using hightemperature high-pressure reaction conditions and to expand the understanding of beryllium nitrides through the characterization of the newly synthesized compounds.

Initially, the existing system of Be-P-N compounds was extended by the synthesis of Be₂PN₃, which enables access to highly condensed, wurtzite-type beryllium nitrides (Chapter 2). Building on this, the previously gained knowledge was used to open the substance class of Be-Ge-N with the synthesis of BeGeN₂. This new compound was compared to its lighter homologue BeSiN₂ in order to investigate differences in synthesis, structure and properties (Chapter 3). With the subsequent synthesis of W₂Be₄N₅ and W₄Be₈N₉, not only the substance class of Be-W-N was opened, but it also creates a starting point for the further exploration of transition metal beryllium nitrides (Chapter 4). Finally, with the synthesis of BeW₁₀N₁₄(N₂), the very first ternary transition metal compound containing [N₂] units was successfully prepared and, in addition, the sought-after motif of BeN₆ octahedra in a nitride was confirmed (Chapter 5).

All reactions were carried out under high-temperature high-pressure conditions. Each structure was elucidated in a combined approach from several analytic techniques: The structural model obtained from single-crystal X-ray diffraction (sc-XRD) or powder XRD was always backed up by additional analytic such as nuclear magnetic resonance (NMR), energy-dispersive X-ray (EDX), inductively coupled plasma (ICP), infrared (IR) or Raman spectroscopy or second harmonic generation (SHG) measurements and/or verified with density functional theory (DFT), MAPLE or CHARDI calculations. Further analytics such as UV/Vis or vibrating sample magnetometer (VSM) measurements completed the characterization of the new compounds. The elastic properties for Be₂PN₃, BeSiN₂, $W_2Be_4N_5$ and $BeW_{10}N_{14}(N_2)$ were examined by DFT calculations or by pressure-volume data derived from compression experiments in a diamond anvil cell (DAC). The isothermal bulk moduli range from $K_0 = 220-370$ GPa and therefore demonstrate a high degree of incompressibility for all compounds.

Beyond that, the nucleus ⁹Be was measured for the first time in a tetrahedral nitride coordination by NMR spectroscopy. Not only the values for δ_{iso} , C_q and η_q of ⁹Be in Be₂PN₃, BeSiN₂ and BeGeN₂ were evaluated, but also the binary Be₃N₂ was analyzed in order to create a reference point. This first collection provides a basis for the evaluation of future beryllium nitrides.

A more detailed summary for each chapter is provided on the following pages.

6.1. Highly Condensed and Super-Incompressible Be₂PN₃

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The first wurtzite-type beryllium nitride, Be₂PN₃, was prepared in a high-pressure high-temperature reaction at 9 GPa and 1500 °C from Be₃N₂ and P₃N₅ (Equation 6.1). It is the missing member in the row of formula type M_2 PN₃ (M = Mg, Zn). The structure was elucidated by powder X-ray diffraction ($Cmc2_1$ (no. 36), a = 8.4610(16), b = 4.8777(6) and c = 4.5691(8) Å, Z = 4). Be₂PN₃ is built up from all-side vertex-sharing



BeN₄ and PN₄ tetrahedra, rendering the compound as a double nitride, rather than a nitridophosphate. The structural model was further corroborated by ⁹Be and ³¹P solid-state nuclear magnetic resonance (NMR) spectroscopy. We present ⁹Be NMR data for tetrahedral nitride coordination for the first time with δ_{iso} = 4.0 ppm for ⁹Be in Be₂PN₃ and δ_{iso} = 5.3 ppm in Be₃N₂, respectively.

$$2 Be_3N_2 + P_3N_5 \to 3 Be_2PN_3$$
 (6.1)

Infrared and energy-dispersive X-ray spectroscopy (FTIR and EDX), as well as temperature dependent PXRD complemented the analytical characterization. Density functional theory (DFT) calculations revealed super-incompressible behavior and the remarkable hardness of this low-density material with K_0 = 228 GPa and H_v = 29 GPa.

6.2. Synthesis and Comprehensive Studies of Be-IV-N₂ (IV = Si, Ge): Solving the Mystery of Wurtzite-Type $Pmc2_1$ Structures

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The synthesis and characterization of BeGeN₂ is presented. It is the first wurtzite-type material crystallizing in space group $Pmc2_1$. The compound was synthesized in a high-pressure high-temperature reaction at 6 GPa and 800 °C starting from Be₃N₂ and Ge₃N₄ (Equation 6.2). Its structure was elucidated in a combined approach of PXRD ($Pmc2_1$ (no. 26), a = 2.98324(5), b =5.11633(8), c = 4.83927(8) Å, Z = 2),



NMR, Raman and energy dispersive X-ray (EDX) spectroscopy as well as MAPLE, CHARDI and DFT calculations. The pressure stabilization of Ge_3N_4 enables the synthesis of this ternary double-nitride. For comparison, the lighter homolog, $BeSiN_2$, was synthesized in a high-temperature reaction at 1900 °C starting from Be_3N_2 and Si_3N_4 (Equation 6.3).

$$Be_3N_2 + Ge_3N_4 \rightarrow 3 BeGeN_2 \tag{6.2}$$

$$Be_3N_2 + Si_3N_4 \rightarrow 3 BeSiN_2 \tag{6.3}$$

Both compounds were further corroborated by temperature-dependent PXRD, second harmonic generation (SHG) and UV/VIS measurements to illustrate the differences and similarities between the two compounds. A phase-transition of BeSiN₂ to the BeGeN₂-type structure was not observed at pressures up to 90 GPa and temperatures > 7800 K. Nevertheless, the experiment allowed the determination of the bulk modulus $K_0 = 374(5)$ GPa, which identifies BeSiN₂ as an ultra-incompressible material.

6.3 Combination of Ambient and High-Temperature Beryllium Nitride Motifs in $W_2Be_4N_5$ and $W_4Be_8N_9$

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The synthesis of the first two transition metal nitridoberyllates is presented. $W_2Be_4N_5$ and $W_4Be_9N_9$ were synthesized in a high-pressure high-temperature reaction at 8 GPa and 1350 °C. To overcome synthetic challenges, a combined approach of high-temperature high-pressure activation of Be_3N_2 and oxidation of tungsten by *in-situ* generated nitrogen was utilized to react the starting materials (Equation 6.4).



The structure of W₂Be₄N₅ was elucidated by a complementing single-crystal XRD ($R\overline{3}m$ (no. 166), a = 2.86870(10), c = 37.0749(13) Å, Z = 3) and elemental analysis, which excluded a structural model due to the stoichiometry. The crystal structure consists of alternating layers of WN₆ trigonal prisms and BeN₄ tetrahedra. The separating nitridoberyllate layers show either ambient temperature (α -Be₃N₂ type) or high temperature (β -Be₃N₂ type) motifs.

$$4 Be_{3}N_{2} + 6 W + 3 NaN_{3} \rightarrow 3 W_{2}Be_{4}N_{5} + 3 Na + N_{2}$$
(6.4)

 $W_2Be_4N_5$ was further corroborated by infrared (IR), nuclear magnetic resonance (NMR) and UV-VIS spectroscopy and vibrating sample magnetometry (VSM) measurements. The latter revealed a mixed valence with an intermediate oxidation state of 3.5 for the W atoms. The second compound, $W_4Be_8N_9$, was obtained for longer dwelling times. Its structure was refined based on those of $W_2Be_4N_5$ and represents a stacking variant of the latter ($R\overline{3}m$; a = 2.8647(3); c = 67.273(7) Å, Z = 3).

6.4 High-Pressure Synthesis of Ultra-Incompressible Beryllium Tungsten Nitride Pernitride BeW₁₀N₁₄(N₂)

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The ternary transition metal nitride $W_2Be_4N_5$ was investigated in a laserheated Diamond Anvil Cell by pressure-dependent synchrotron Xray diffraction. The evaluation of the pressure-volume data with a 2nd order Birch-Murnaghan equation of state returns an isothermal bulk modulus $K_0 = 273.4(2)$ GPa. At a pressure of 41 GPa the sample was heated to induce a phase transition to the first ternary transition metal



pernitride, BeW₁₀N₁₄(N₂). Its structure was solved and refined by single-crystal synchrotron X-ray diffraction (*C*2/*m* (no. 12), *a* = 19.803(5), *b* = 2.7867(6), *c* = 8.2467(15) Å and β = 99.605(19)°, *Z* = 2). The crystal structure unites commonly encountered structural motifs like WN₇ capped trigonal prisms with unprecedented BeN₆ octahedra and (N₂) anions. Elastic and electronic properties of the title compound were corroborated by DFT calculations revealing ultra-incompressible behavior with *K*₀ = 337 GPa and metallic properties at the same time.

The title compound is discussed in the context of fundamental nitride and pernitride chemistry, as six-fold N-coordinated Be had been a very rare structural motif. $BeW_{10}N_{14}(N_2)$ is quenchable to ambient pressure conditions and thus enables further examinations. This gives hope for the synthesis of a model compound for the nitrogen fixation process in the enzyme nitrogenase.

7 Discussion and Outlook

Chapter 2–4 focused on the synthesis of novel beryllium nitrides using a large volume press (LVP). Four new compounds were introduced: Be_2PN_3 , $BeGeN_2$, $W_2Be_4N_5$ and $W_4Be_8N_9$. Chapter 5 presented the first synthesis of a ternary transition metal nitride with dinitrogen anions, namely $BeW_{10}N_{14}(N_2)$ in a diamond anvil cell. The following sections discuss the progresses in beryllium nitride synthesis and analysis (Section 7.1) and in the understanding of beryllium nitrides at high-pressures (Section 7.2) and integrate the results of Chapter 2–5 in a larger context. The results are not reiterated in detail, as they are summarized in Chapter 6.

7.1 Progress in Beryllium Nitride Synthesis and Analysis

Chapter 1.3 depicted in detail the several challenges, which come along with the syntheses of beryllium nitrides. These syntheses are not carried out using conventional approaches, but by means of activation by reactive starting materials (such as Li_3N) or thermal activation or a combination of both. As a result, compounds consisting of thermally labile nitrides, such as Ge_3N_4 or P_3N_5 , have hardly been researched. One exception is phe-BeP₂N₄, which was synthesized by the combination of high-temperature activation of Be₃N₂ and high-pressure stabilization of P_3N_5 .^[1]

This combined approach has been developed further in Chapter 2 and 3 on the example of the synthesis of highly condensed, wurtzite-type compounds. The optimal synthesis conditions range from 6–9 GPa and 800–1500 °C. Higher pressures are conceivable, whereas lower temperatures seem unlikely without the addition of a very reactive partner. The opposite, lower pressures and higher temperatures is unfavorable as it fosters the decomposition of the thermally labile starting materials. Two new compounds were synthesized in the large volume press by the high-temperature high-pressure (HT/HP) approach, namely Be₂PN₃ and BeGeN₂. This extended the class of beryllium phosphorus nitrides and opened up the class of beryllium germanium nitrides.

In addition, the HT/HP approach has succeeded in opening the door to the class of transition metal beryllium nitrides on the example of $W_2Be_4N_5$ and $W_4Be_8N_9$. What is remarkable about these compounds is the synthesis starting from two inert starting materials at the same time, namely Be_3N_2 and W. While the first can be activated in a radiofrequency furnace at high-temperature conditions (see Chapter 3), tungsten is the standard crucible material under such conditions and cannot usually be made to react with elemental N_2 .^[2] Nevertheless, a synthesis was possible by using the HT/HP approach: The increased oxidation potential of N_2 under pressure is sufficient to oxidize W and to react with the thermally activated Be_3N_2 . Since no elemental nitrogen can be loaded into the LVP, NaN_3 or NH_4N_3 were used as sources and N_2 was generated *in-situ*, which may further increase its reactivity. This synthesis method lays the basis for the future exploration of transition metal beryllium nitrides. This applies both to elements that react easily with N_2 , such as Fe or Ti, and to elements that are difficult to oxidize, such as Mo.

If the results from chapter 2–5 are included, an updated periodic table of the elements with ternary beryllium nitrides can be drawn up (Figure 7.1).

н																	He
Li	Be											В	С	N	0	F	Ne
Na	Mg											AI	Si	Р	S	Cl	Ar
к	Ca	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Υ	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	Ι	Xe
Cs	Ва	La	Hf	Та	w	Re	Os	Ir	Pt	Au	Hg	ΤI	Pb	Bi	Ро	At	Rn

Figure 7.1. Periodic table of elements with none (white), one (red), two (green) or three (orange) ternary beryllium nitrides. Split boxes indicate the status before and after this thesis.

Utilizing the HT/HP approach, it was possible to expand the number of beryllium nitrides, but there are still unexplored areas in the periodic table (Figure 7.1). The successful synthesis of a ternary beryllium nitride with elements of the third main group is still pending. A synthesis does not appear impossible since a quaternary compound, Sr₂[BeAl₃N₅], already exists.^[3] However, Sr₂N is used as very reactive starting material in its synthesis and thus could influence the activation of Be₃N₂ and AlN significantly. For the synthesis of a fictitious ternary compound, e.g. Be₃BN₃, Be₃AlN₃ or Be₃GaN₃, the high thermodynamic stability of BN, AlN or GaN must be considered. A synthesis route using NH₃, e.g. produced *in-situ* by the decomposition of NH₄N₃, could provide suitable reaction conditions. A similar observation was made for BeGeN₂ (Chapter 3): Syntheses using NH₄N₃ contained a significantly higher phase fraction of BeGeN₂ and were more crystalline. The ammonothermal method, which is of great importance for the synthesis of GaN, could also be successful here.^[4] However, such an experiment must be carried out under extremely strict safety measures, as the container is pressurized and in the event of a leak, beryllium would be finely distributed in the laboratory.

Other white spots remain for the heavier alkali beryllium nitrides. Their synthesis could be achieved by using the respective azide (NaN₃, KaN₃, RbN₃ or CsN₃) and Be or Be₃N₂ under HT/HP conditions. It is also noticeable that there is no ternary oxynitride of Be so far. In the presence of oxygen during the synthesis of Be₃N₂, no beryllium oxynitride, e.g. Be₄N₂O, is formed, but Be₃N₂, which is contaminated with BeO. This is probably caused by the high thermodynamic stability of the binary compounds. However, we know from the example of sinoite, Si₂N₂O, that under extreme conditions, as occurring in chondrite meteorites, ternary oxynitrides can be formed.^[5]

All above mentioned compounds synthesized in the LVP exhibit BeN₄ tetrahedra as their basic building block, which can be connected to 3D networks by vertex-sharing (Be₂PN₃, BeGeN₂) or, as in the case of W₂Be₄N₅ and W₄Be₈N₉, by edge-sharing forming layers. The structural motif of BeN₃ triangles was not observed, what is in line with the pressure-coordination rule.^[6] However, the tetrahedral motif is not exclusively for high-pressure conditions as it also occurs in Be₃N₂ itself or MgBe₂N₂.^[7-10]

As part of this work, the chemistry of beryllium nitrides was also investigated at pressures above 40 GPa using a DAC. Up to now, investigations with this method have been limited to sp-BeP₂N₄ and BeN₄.^[11-12] By synthesizing BeW₁₀N₁₄(N₂) from W₂Be₄N₅ in a DAC at a pressure of 42 GPa, the first ternary transition metal pernitride was produced which even contains BeN₆ octahedra. This is remarkable for several reasons: First, this uncommon coordination polyhedron for Be was so far only known in the polynitride BeN₄. In BeW₁₀N₁₄(N₂) it is, however, not stabilized by [N₂] dimers but by nitride anions. This is astonishing since N³⁻ ions have a higher charge and, therefore, a greater Coulomb repulsion than polynitride anions. Second, the edge linkage of the octahedra creates a new structural motif that has not yet been observed. Third, the synthesis was conducted at a significantly lower pressure than previously with BeN₄ (84 GPa).^[12] This is in line with the recent results of *Spar et al.* on BeO₆ octahedra at approx. 40 GPa.^[13] At lower synthesis pressure, the diamonds can be reused after the experiments, thus reducing the costs and allowing more experiments and therefore systematic research. All these reasons underline the importance of future HP/HT investigations on beryllium nitrides in diamond anvil cells.

The combination of several analytical techniques has proved successful in elucidating the structure of the newly discovered compounds. From XRD data, received from single crystals or powders, a first structural model could be derived. However, these structural models are prone to errors, as the atomic form factor of Be is small compared to the one of heavy atoms and the coordination polyhedra of the Be atoms and their linkage is not always unambiguous. The verification of the structural model by ⁹Be NMR has proven to be very useful and is also recommended for future structural elucidation. The collection of the first NMR parameters i.e. values for δ_{iso} , C_q and η_q of ⁹Be in a nitride, tetrahedral coordination creates a first set of reference points. To back up the structural model, an additional chemical analysis, such as ICP-OES is recommended, to determine the ratio of other metals to beryllium. This is in most cases the better alternative to EDX, with which Be can usually not be detected. Vibrational spectroscopic investigations such as IR or Raman in combination with DFT calculations confirm the structural model and can exclude N-H bonds. Where verification by NMR was not possible, e.g. due to the small amount of samples obtained from DAC experiments, DFT calculations have proven to be extremely useful. Nevertheless, this should remain the exception and should only be used as a supportive tool. NMR investigations in DACs have been further developed in recent years, so that they can possibly not only be used in special experiments but also by experimental chemists to investigate newly synthesized compounds in the future.^[14]

7.2 Combining Beryllium and Nitrogen at High-Pressure Conditions

As depicted in the Introduction (Section 1.2), beryllium nitrides are expected to yield new structures with extraordinary properties. That the high-pressure high-temperature approach is a promising one to overcome common barriers in the synthesis of beryllium nitrides was discussed in Section 7.1. So, what about the structures and properties?

All the materials presented in this dissertation are not just compounds that happen to combine the elements beryllium and nitrogen and in which the elements could be replaced by others. Rather, the targeted combination of Be and N leads to the unique properties of the discovered compounds. This is discussed for every found compound, shortly and summarized in Figure 7.2.



Figure 7.2. Unique properties of the found compounds caused by the targeted combination of Be and N: High covalent bonding character and resulting hardness, as shown on the example of Be₂PN₃ (A), specific ratio of ionic radii in BeGeN₂ leading to the unprecedented wurtzite-type structure in space group *Pmc*2₁ (B), highly condensed layers with edge-sharing tetrahedra in W₂Be₄N₅ (C) and the stabilization of the theoretically [W₁₀N₁₆] framework through the incorporation of Be forming the first ternary transition metal pernitride BeW₁₀N₁₄(N₂) (D).

Chapter 2 describes that a sample of wurtzite-type Be_2PN_3 can scratch a tungsten carbide mortar ($H_v = 27$ GPa) due to its high hardness.^[15] This experimental observation is confirmed by DFT calculations, revealing an isothermal bulk modulus of $K_0 = 228$ GPa and a Vickers hardness of $H_v = 29$ GPa. These mechanical properties of the material are most likely due to the strong, covalent Be-

N bond and the high degree of condensation of $\kappa = 1$. Only a combination of both, covalent bonding and high degree of condensation build the basis for incompressibility and hardness. The comparison with BeO ($H_v = 13$ GPa),^[16-17] which also crystallizes in a wurtzite-type structure, shows that the introduction of nitrogen improves the mechanical properties. However, Be²⁺ cannot be replaced just by Mg²⁺ or Zn²⁺ as found in Mg₂PN₃ or Zn₂PN₃.^[18] Although both are isostructural to Be₂PN₃, the electronegativity of e.g. Mg is significantly lower and, therefore, the character of the Mg-N is less covalent. A direct example of the strong polarization of Be compared to Mg was recently provided by *Buchner et al.* who were able to show in a complex with Be-Mg bonding that the bond is polarized to the Be atom.^[19] However, a high covalent bonding alone is not sufficient for high mechanical resistance. This is clearly illustrated by the example of the two carbon allotropes graphite and diamond, which both have covalent bonds. However, a rigid structure is only formed by linking the atoms to form a 3D network. Therefore, just the combination of Be and N in this wurtzite-type composition enables the high mechanical properties. This is also supported by the investigation of the elastic properties of wurtzite-type BeSiN₂ in a diamond anvil cell, which revealed a bulk modulus of $K_0 = 374(5)$ GPa and renders BeSiN₂ as an ultra-incompressible material.

BeGeN₂ is the first wurtzite-type material that crystallizes in space group $Pmc2_1$ and thus describes a new structure type. As explained in detail in Chapter 3, the unique ratio of ionic radii is responsible for this. Only the combination of Be²⁺ (0.27 Å) and Ge⁴⁺ (0.39 Å) lead to a ratio of 0.69.^[20] In this case, the presence of all three elements is crucial: Neither Be²⁺ can be replaced by other divalent, tetrahedron-forming cations such as Mg²⁺ or Zn²⁺, nor Ge⁴⁺ by Si⁴⁺, since BeSiN₂ and II-IV-N₂ (II = Zn, Mg; IV = Si, Ge) all crystallize in space group $Pna2_1$ and thus in the β -NaFeO₂ structure type.^[21-23] To bring the cations of Be and Ge together in a ternary compound in a 1:1 ratio, N³⁻ ions are necessary to guarantee charge neutrality and cannot be replaced by oxide anions in a wurtzite-type structure. Further investigations by other researchers suggest that BeGeN₂ is the only compound that can crystallize intrinsically in $Pmc2_1$.^[24] Nevertheless, other II-IV-N₂ compounds in space group $Pmc2_1$ could be synthesized using a seed crystal of BeGeN₂. Another special feature is that, although Be forms intermetallic phases with many metals, there are no binary compounds with Ge to date. Nitrogen is the "cement" that holds these two elements together in BeGeN₂.

While Be₂PN₃ and BeGeN₂ both consist of all-side vertex sharing tetrahedra and thus assemble a 3D network of BeN₄ tetrahedra, W₂Be₄N₅ and W₄Be₈N₉ exhibit only edge-sharing BeN₄ tetrahedra. Both crystal structures consist of alternating layers of WN₆ trigonal prisms and BeN₄ tetrahedra. The separating nitridoberyllate layers show either ambient temperature (α -Be₃N₂ type) or high-temperature (β -Be₃N₂ type) motifs. The combination of ambient and high-temperature motifs in one compound is so far uncommon in beryllium nitrides but enables the synthesis of unprecedented structures. The high degree of condensation within these layers could be the reason for the relatively high bulk modulus of K_0 = 273.4(2) GPa of W₂Be₄N₅ and its resistivity against diluted HCl, NaOH and H₂O₂.

Finally, the synthesis of BeN₆ octahedra in BeW₁₀N₁₄(N₂) is a great success. This uncommon structural motif was so far only known in the polynitride BeN₄. In BeW₁₀N₁₄(N₂) it is however not stabilized by polynitride anions but by nitride anions. DFT calculations demonstrate that the intercalation of Be²⁺ in these channels is highly preferred by $\Delta H = -5.348$ eV per unit cell (256 kJ/mol) and stabilizes the structure. It can be assumed that the combination of pernitride units and BeN₆ octahedra in the voids is responsible for the high bulk modulus of $K_0 = 337$ GPa and thus ultra-incompressible behavior.

For all compounds, their unique properties arise from the combination of Be and N. Therefore, research into further, new ternary beryllium nitrides should also produce unexpected structures

with intriguing properties. Especially further experiments in laser heated diamond anvil cells could raise the number of structures with BeN_6 octahedra and could enable a systematic study of this structural motif.

7.3 Where to go from here?

The scope of this thesis was to synthesize new ternary beryllium nitrides, open new compound classes and to systematically expand our understanding of beryllium nitrides. In particular, the method of high-pressure synthesis was further developed. Looking at the updated periodic table of elements with ternary beryllium nitrides (Figure 7.1), it becomes clear that there is still a lot to do. By explorative research using the high-temperature high-pressure approach in a large volume press, it seems promising that many more compounds with unprecedented structures and intriguing properties can be synthesized. The synthesis of the first Be-III-N compound as well as the synthesis of further alkali metal beryllium nitrides could be the next steps learning more about beryllium nitrides. However, there should be no limits to creativity when combining different elements. My personal advice is not to stick to a particular compound (class), but to explore a broad range of different elemental combinations.

Further investigations using diamond anvil cells will certainly hold the biggest surprises. Several questions are linked to experiments under high-pressure conditions: Is there a trigonal bipyramidal coordinated BeN₅? What connectivity patterns between BeN₆ octahedra are possible? Are there compounds with BeN₄ and BeN₆ octahedrons at the same time? The co-existence of several structural motifs such as BeN₃ triangles and BeN₄ tetrahedra, for example in Eu₃Be₂₂N₁₆O, is known.^[25] But does this also apply under elevated pressure?

Besides the exploration under high-temperature high-pressure conditions there are more fields to discover. Many Be-containing compounds were examined only by quantum mechanical calculations so far, for example the class of ternary beryllium phosphides. The interest in such compounds is high as many theory papers predict semiconducting properties, making them interesting for optoelectronic applications such as photodetectors or solar cells.^[26-30] So far, however, there is no experimental proof of the existence of such compounds. The synthesis of BeSiP₂ or BeGeP₂ seems conceivable, even without the use of high-pressure conditions.

Parallel to the progress in experimental exploration, the NMR spectroscopy on nucleus ⁹Be should be further developed in order to improve the structure solution process. The investigation of ⁹Be in BeN₆ octahedra by NMR spectroscopy, conducted in a diamond anvil cell would be a further milestone in this field.^[14]

The element beryllium was discovered over 200 years ago by Louis-Nicolas Vauquelin.^[31] While many other elements have already been studied very well, Be has been sorely neglected. The interdisciplinary results of research in recent years show that we are only just beginning to understand the chemistry of this main group element.

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8 Appendix

8.1 Supporting Information for Chapter 2

Experimental Procedures

Safety notice

Beryllium and its compounds can cause different diseases like the acute berylliosis, the chronic beryllium disease (CBD), contact dermatitis and cancer. Especially the inhalation of Be containing dust or the contact to solvable Be salts is dangerous. Consequently, the complete handling of starting materials and Be containing samples was carried out in a designated glovebox. Samples outside the glovebox were only transported in closed vessels. For unavoidable work with Be outside the glovebox (e.g. cleaning working equipment) care must be taken to additional safety precautions like FFP3-mask and the avoidance of dusts. Guidelines how to work with Be are available in the literature.^[1-2]

Preparation of starting materials

Be₃N₂ was synthesized by the reaction of elemental Be in a N₂ atmosphere.^[3] Beryllium flakes (ABCR, 99+%) were crushed in a tungsten carbide mortar, filled into a tungsten crucible and reacted in a radiofrequency furnace (8TIG 10/100; Hüttinger Elektronik Freiburg, Germany). The sample was heated to 1500 °C within 10 minutes, dwelled at this temperature for 10 h and cooled down to room temperature within 1 h. Phase purity was confirmed by means of powder X-ray diffraction (PXRD).

Partially crystalline P_3N_5 was synthesized by the ammonolysis of P_4S_{10} (Acros Organics, >98%) according to Stock et al.^[4] The starting material was filled in a quartz tube and saturated with dry ammonia for 4 h at room temperature. Under a flow of dry ammonia the furnace was heated up to 850 °C with a rate of 7 °C/min, held there for 4 h and cooled down to ambient temperature with a rate of 7 °C/min. The orange product was washed with conc. HCl and de-ionized water and dried at 100 °C. Phase purity was confirmed by means of PXRD and CHNS analysis (calc. (%) C 0, H 0, N 42.98, S 0; found (%): C 0, H 0, N 42.70, S 0).

High-pressure high-temperature synthesis

Be₂PN₃ was synthesized in a high-temperature high-pressure approach in a hydraulic 1000 t press using the multianvil technique with a modified Walker module.^[5-6] To prevent oxygen exposure and hydrolysis and because of safety reasons (see above), the starting materials were handled in an Arfilled glovebox (Unilab, MBraun, Garching; O₂, H₂O < 1 ppm). Stoichiometric amounts of Be₃N₂ (28.2 mg, 0.51 mmol) and P₃N₅ (41.8 mg, 0.27 mmol) were ground in a tungsten carbide mortar and packed in an h-BN crucible (Henze, Kempten). The latter was placed in the center of two graphite furnaces with two MgO spacers, closed with a cap of h-BN and transferred in a ZrO₂ cylinder. The furnaces were contacted with Mo plates. The whole sleeve was placed in the center of a drilled MgO octahedron (5% Cr₂O₃ doped MgO, 18 mm edge length, Ceramic Substrates & Components Ltd, Isle of Wight). The octahedron was placed in the void of eight tungsten carbide cubes with truncated corners, which were separated with pyrophyllite gaskets. The assembly was transferred to the multianvil apparatus and compressed to 9 GPa within 240 min. At this pressure the sample was heated to 1450 °C within 60 min, dwelled at this temperature for 180 min and cooled down to room temperature within 60 min before the pressure was decreased to ambient pressure within 720 min.

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy

For electron microscope investigations, the sample was positioned on a self-adhesive carbon foil and coated with carbon using an electron beam evaporator (BAL-TEC MED 020, BalTec AG, Pfäffikon) to guarantee electrical conductivity. For SEM imaging and EDX measurements a Dualbeam Helios Nanolab G3 UC (FEI, Hilsboro) equipped with an X-Max 80 SDD detector (Oxford instruments, Abingdon) was used. The data was processed with the Aztec software.^[7] The accelerating voltage for SEM imaging and EDX measurements was 5.0 kV.

Solid state magic-angle spinning (MAS) NMR spectroscopy

For solid state NMR measurements, the sample was ground and loaded in a ZrO_2 rotor with an outer diameter of 2.5 mm. Tightly packed Teflon tape was used as spacer at the bottom and the top of the rotor to avoid direct contact of the Be-containing sample with the environment. NMR spectra were collected at 10 kHz spinning frequency on an Avance III 500 spectrometer (Bruker, Karlsruhe) with a 11.7 T magnet (500.25 MHz ¹H frequency).

Due to the nuclear spin of ⁹Be (I = 3/2) quadrupolar interactions have to be taken into account for the evaluation of the measured data. Hence, the central transition was fitted with the program DMFIT to elucidate the values for the isotropic chemical shift (δ_{iso}), the quadrupolar coupling constant (C_q) and the asymmetry parameter (η_q).^[8]

Additional spectra of ⁹Be were measured from self-synthesized Be_3N_2 (see above) and BeO (Alfa Aesar, 99.95%). All spectra were indirectly referenced to ¹H in 100% tetramethylsilane (TMS) at -0.1240 ppm.

Temperature dependent powder X-ray diffraction (HT-PXRD)

The thermal behavior of Be₂PN₃ was investigated by temperature-dependent powder X-ray diffraction. The ground sample was loaded into a silica capillary (Hilgenberg, Malsfeld) with an outer diameter of 0.3 mm and heated under Ar atmosphere from 50 to 900 °C in steps of 50 °C with a rate of 10 °C/min. Following, the sample was cooled to 50 °C with the same rate and step size. After each temperature step during heating and cooling, powder diffraction patterns were collected within 1.5 h at constant temperature on a STOE Stadi P diffractometer (STOE & Cie GmbH, Darmstadt, Ag-K α_1 radiation, λ = 0.55942 Å, Ge(111) monochromator, IP-PSD detector) equipped with a STOE resistance graphite furnace. For every diffraction pattern a Rietveld refinement were conducted to determine the lattice parameters and the cell volume. The so obtained data were plotted and fitted with Origin to determine the thermal expansion parameter α .^[9]

Powder X-ray diffraction (PXRD), structure solution and Rietveld refinement

Powder X-ray diffraction data (PXRD) was collected on a STOE Stadi P diffractometer (STOE & Cie GmbH, Darmstadt) in a modified Debye-Scherrer geometry with Ag-K α_1 radiation (λ = 0.55942 Å) equipped with a MYTHEN 1K strip detector and a Ge(111) monochromator. The sample was ground and sealed in a glass capillary (0.3 mm outer diameter, Hilgendberg, Malsfeld) and centered on a rotating goniometer head in the beam.

All steps for the structure solution were carried out with TOPAS Academic.^[10] First, the diffraction pattern was indexed and the metric was determined to orthorhombic *C*-centered with the lattice parameters a = 8.4506, b = 4.8819 and c = 4.5723 Å. Following, the diffraction pattern was fitted with a Pawley-Fit to generate the list of hkl indices. Via Charge Flipping, the starting model for the Rietveld refinement was obtained.^[11] Lattice parameters and fractional coordinates were freely refined. The site occupancies were freely refined one after the other, but not all at the same time. The value for the isotropic thermal expansion was set to a value comparable to those in other nitridophosphates solved from PXRD data like MgP₈N₁₄, CaP₈N₁₄ or Zn₂PN₃.^[12-14] A second Rietveld-refinement was started from the model of related Mg₂PN₃, but the refined model from charge flipping data fits better to the diffraction pattern. The reason might be the bigger distortion of MgN₄ tetrahedra in Mg₂PN₃. (figure S3)^[15]

The peak profiles were described with the fundamental parameter approach. A potential preferred orientation of the crystallites was accounted for with a 4th order harmonic function and the background was modeled by a shifted Chebyshev polynomial.^[16-17] The results were plotted using Origin.^[9] Structures were visualized using VESTA.^[18]

Fourier transformed infrared spectroscopy (FTIR)

An infrared spectrum of the sample was collected on a Bruker Alpha II FTIR spectrometer using a diamond attenuated total reflectance (ATR) unit. The spectrum was recorded in a glovebox in the range of 450–4000 cm⁻¹ and with a resolution of 2 cm⁻¹.

Density functional theory (DFT) calculations

First principle electronic structure calculations were performed with the Vienna ab initio simulation package (VASP) based on periodic density functional theory calculations.^[19-21] Core and valence electrons are separated exploiting projector-augmented waves (PAW).^[22-23] The exchange and correlation energy is calculated using the generalized gradient approximation (GGA), as described by Perdew, Burke and Ernzerhof (PBE).^[24] A more detailed analysis of the band gap was achieved by comparing results using PBE and PBEsol^[25] with results using the meta-GGA functionals modified Becke-Johnson (mBJ)^[26-27], local MBJ (LMBJ)^[28-29], and "regularized-restored strongly constrained and appropriately normed" (r2SCAN)^[30]. Non-spherical contributions to the gradient of the density in the PAW spheres where included when using meta-GGAs. Elastic tensors were determined by performing finite distortions and deriving the elastic constants from the strain-stress relationship. The bulk modulus was calculated using the Voigt-Reuss-Hill approximations,^[31-33] and energy vs. volume calculations. The energy versus volume data was computed by scaling the cell parameters from 93 to 107 % (with a fixed *a:b:c* ratio). The Brillouin zone was sampled on a 9x9x9 Γ-centered

k-point grid and the interpolation of the *k* space was done via the tetrahedron method with Blöchl corrections. The energy convergence criterion was set to 10^{-7} eV and the residual atomic forces were relaxed until the convergence criterion of 10^{-5} eV/Å was reached. The optimization was performed via RMM-DIIS^[34] and a plane wave energy cutoff of 520 eV with full ionic degrees of freedom, i.e. atomic positions, cell shape and cell volume. Both Hellmann-Feynmann forces and stress tensors were calculated. An optimization without symmetry preserves the space group *Cmc2*₁. Phonon calculations were carried out after structural electronic relaxations with VASP using the supercell approach (4 x 4 x 4) at the Γ -point only. Force sets and lattice vibrations were subsequently calculated with PHONOPY.^[35] The resulting phonon band structure and phonon density of states are shown in Figure S9.

Results and Discussion

SEM images and EDX measurements



Figure S2.1. Additional image of polycrystalline Be₂PN₃.

EDX measurements were carried out on different crystallites of Be_2PN_3 (table S1). No other elements than Be, P, N and O were detected. The content of O can be attributed to surface hydrolysis, taking into account that at acceleration voltage of only 5 kV the interaction volume is rather small and surface effects become more prominent. The normalized ratio (Be : P : N = 1.9 : 1.0 : 2.4) is in very good agreement to the theoretical values (Be : P : N = 2 : 1 : 3), considering the precision of the method for light elements.

Table S2.1. EDX measurements of Be_2PN_3 . Results are given in atomic percent with standard deviations in parenthesis.

Measurement	Ве	Р	Ν	0
1	37	18	40	5
2	35	18	42	6
3	30	21	46	2
4	36	16	45	3
5	35	17	45	4
Average	35(2)	18(1)	44(2)	4(2)
Normalized	1.9(1)	1.0(1)	2.4(1)	0.2(1)
Theoretical	2	1	3	0

Structure determination and Rietveld refinement



Figure S2.2. Result of the Rietveld refinement of Be₂PN₃. Observed (black crosses), calculated (red line) powder X-ray diffraction patterns Ag-K α_1 ($\lambda = 0.55942$ Å) and difference plot (grey line). Positions of Bragg reflections of Be₂PN₃ are given as black bars. Although, the amount of WC is too small for a stable refinement, the Bragg reflections are visible. The positions of those are given with blue bars.^[36] Bragg reflections of an unidentified impurity are marked with asterisks.

Formula	Be ₂ PN ₃
Crystal system	orthorhombic
Space group	<i>Cmc</i> 2 ₁ (no. 36)
Lattice parameters / Å	<i>a</i> = 8.4610(16)
	<i>b</i> = 4.8777(6)
	<i>c</i> = 4.5691(8)
Cell volume /ų	188.57(5)
Formula units per unit cell	4
Density / g cm ⁻³	3.208
Molecular weight / g mol ⁻¹	91.02
Diffractometer	Stoe Stadi P
Radiation	Ag-Kα ₁ (λ = 0.55942 Å)
Detector	Mythen 1K
Monochromator	Ge(111)
2θ range / °	1.0 < 2 <i>θ</i> < 40.180
Step width / °	0.015
Data points	2613
Total number of reflections	110
refined parameters	45
Background function	Shifted Chebyshev
Number of background parameters	12
Goodness of fit	2.117
R _p ; R _{wp}	0.065; 0.085
R _{exp} ; R _{bragg}	0.031; 0.027

 $\label{eq:s2.2.} \mbox{Crystallographic data of Be_2PN_3 from Rietveld refinement. Standard deviations are given in parenthesis.}$

Table S2.3. Wyckoff positions, coordinates, isotropic thermal displacement parameters and occupancy of Be₂PN₃. Standard deviations are given in parenthesis.

Atom	Wyck.	x	у	Z	U _{eq} / Å	Occ.
P1	4 <i>a</i>	0	0.1700(11)	0.016(4)	0.009	1
Be1	8 <i>b</i>	0.332(2)	0.165(4)	0.021(13)	0.009	1
N1	8 <i>b</i>	0.337(2)	0.166(3)	0.3994(13)	0.009	1
N2	4 <i>a</i>	0	0.159(3)	0.422(3)	0.009	1

Atom1 - Atom2	Distance / Å	Atom1 - Atom2	Distance / Å
Be1 – N1	1.7079(2)	P1-N1	1.6828(3)
Be1 – N1	1.7378(3)	P1-N1	1.6828(3)
Be1 – N1	1.7303(4)	P1 – N2	1.6624(2)
Be1 – N2	1.7229(3)	P1-N2	1.8536(4)

Table S2.4. Interatomic distances in Be_2PN_3 from Rietveld refinement. Standard deviations are given in parenthesis.

Table S2.5. Interatomic angles of Be_2PN_3 from Rietveld refinement. Standard deviations are given in parenthesis.

Atoms	Angle / °	Atoms	Angle / °	Atoms	Angle / °
N2 – P1 – N2	103.394(4)	N1 – Be1 – N2	103.839(4)	Be1 – N1 – Be1	108.826(4)
N1 – P1 – N2	109.387(4)	N1 – Be1 – N1	109.877(4)	Be1 – N1 – Be1	107.361(5)
N1 – P1 – N2	109.387(4)	N1 – Be1 – N2	111.298(6)	Be1 – N1 – Be1	108.837(6)
N1 – P1 - N1	110.149(12)	N1 – Be1 – N2	111.047(12)	Be1 – N2 – Be1	111.611(12)
N1 – P1 – N2	109.387(14)	N1 – Be1 – N1	108.994(4)	Be1-N1-P1	111.606(6)
N1 – P1 – N2	112.140(6)	N1 – Be1 – N1	111.497(6)	Be1-N2-P1	104.312(4)
P1 – N2 – P1	106.708(3)				

DFT optimization of the structural model

Table S2.6. Differences between the atomic positions of Be_2PN_3 as obtained from Rietveld refinement and the structural model received from DFT optimization.

Atom	Wyck.	Δx	Δy	Δz
P1	4 <i>a</i>	0	-0.0064	0.0027
Be1	8 <i>b</i>	0.0027	0.0037	-0.0093
N1	8 <i>b</i>	-0.0028	0.0037	-0.0093
N2	4 <i>a</i>	0	0.0095	0.0361

The structural model of Be_2PN_3 as obtained from Rietveld refinement was optimized via DFT calculations and afterwards compared via the Bilbao Crystallographic Server.^[37] Both, a very small degree of lattice distortion of 0.0020 and a maximum difference between the atomic positions of the matching atoms of 0.1722 Å, underline the experimental evaluated model.

Comparison of Be₂PN₃ to Mg₂PN₃



Figure S2.3. Structure comparison of Be₂PN₃ to Mg₂PN₃. Both compounds crystallize in a wurtzite structure type. However, the structure of Mg₂PN₃ is more distorted due to a bigger cation size, leading to a longer Mg-N distance compared to Be-N and P-N (average bond lengths: Mg-N: 2.1043 Å, Be-N: 1.7247 Å, P-N: 1.7204 Å). a) Crystal structure of Be₂PN₃. B) Crystal structure of Mg₂PN₃. (Be: green, Mg: orange, P. brown, N: blue).

FTIR spectrum



Figure S2.4. FTIR spectrum of Be_2PN_3 . No N–H valence bonds are visible. Absorption bands in the fingerprint region (< 1000 cm⁻¹) originate from the Be/P/N-framework.

HT-PXRD



Figure S2.5: Temperature dependent powder X-ray diffraction pattern (Ag-K α_1 radiation, $\lambda = 0.55942$ Å) measured under Ar atmosphere showing a slight expansion of the lattice parameters with increasing temperature, but neither a decomposition or phase transition of Be₂PN₃ up to 900 °C. However, starting at 700 °C, additional, very weak reflections can be observed, that might arise from the crystallization of a previously amorphous side phase.



Figure S2.6: Temperature-dependent evolution of the cell volume and the lattice parameters of Be₂PN₃ with linear fits. ($\alpha_o = 7.6(3)$; $\alpha_b = 6.4(3)$; $\alpha_c = 5.5(3)$; $\alpha_V = 19.7(5)$ ppm K⁻¹).





Figure S2.7: Solid state MAS NMR spectra of ⁹Be and ³¹P of Be₂PN₃ (a, b), Be₃N₂ (c, d) and BeO (e, f) each at a spinning frequency of 10 kHz. Spinning side-bands are marked with asterisks. a) ⁹Be spectrum of Be₂PN₃ shows one narrow signal. The spectrum shows no other Be signal. b) ³¹P spectrum of Be₂PN₃ with an isotropic chemical shift value of the main signal of 43.4 ppm. The smaller signal at 49.4 ppm may arise from an amorphous side phase. c) ⁹Be spectrum of Be₃N₂ with one Be signal. d) Fit of the spectrum shown in c) to obtain values for the isotropic chemical shift δ_{iso} and for the magnitude of the quadrupolar interaction. e) ⁹Be spectrum of BeO. f) Fit of the spectrum shown in e) to determine the chemical shift δ_{iso} and the magnitude of the quadrupolar interaction.

Charge distribution (CHARDI)

Table S2.7. Results of the CHARDI analysis for Be₂PN₃. All effective coordination numbers and the mean total charges are in good agreement with the theoretical values.

Tetrahedron	Be N1 N1 N1 N2	P/Be N2 N2 N3 N3
Average bond length / Å	1.7247	1.7204
Polyhedral volume / Å ³	2.6243	2.6024
Distortion index (bond length)	0.00539	0.03872
Quadratic elongation	1.0022	1.0048
Bond angle variance / ° ²	8.4069	10.3311
Effective coordination number	3.9942	3.7272
Total charge (theory)		
Ве	2.018 (2.000)	-
Р	-	4.963 (5.000)
N1	-2.908 (-3)	-2.908 (-3)
N2	-3.184 (-3)	-3.184 (-3)

MAPLE

Table S2.8: Results of MAPLE calculations show a difference of 1.3% in the Madelung part of lattice energy for Be_2PN_3 compared to the sum of the respective binary nitrides Be_3N_2 and P_3N_5 .

	2 Be ₃ N ₂ + P ₃ N ₅	\rightarrow	3 Be ₂ PN ₃	
α -P ₃ N ₅	78531 kJ mol ⁻¹	Be_2PN_3	3 x 38916 kJ mol ⁻¹	
α -Be ₃ N ₂	2 x 19876 kJ mol ⁻¹			
	118283 kJ mol ⁻¹		116748 kJ mol ⁻¹	1.3% difference

DFT calculation



Table S2.9. Bandgaps as extracted from DFT calculations of Be₂PN₃ with different exchange functionals.

Figure S2.8. Plot of energy vs. volume, data received from scaling the cell parameters for Be_2PN_3 . Energy from PBE calculations shown with black dots. The corresponding fit (red line) was extracted via the universal equation of states as described by Vinet et al.^[38]

Table S2.10. Elastic properties of Be_2PN_3 as obtained from bulk modulus calculations via the 6x6 elastic tensors.^[39]

Be ₂ PN ₃	K / GPa	G / GPa	<i>E /</i> GPa	HV / GPa
PBE	218.0	183.4	429.7	28.0
PBE + VDW	230.0	191.6	449.9	28.7
SCAN	237.4	201.0	470.2	31.0



Figure S2.9. Projected phonon band structure for Be_2PN_3 calculated from supercells (4 x 4 x 4) within the VASP program and evaluated by PHONOPY. The absence of negative vibrational modes confirms the stability of the optimised structure of Be_2PN_3 .

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8.2 Supporting Information for Chapter 3

Experimental Procedures

Safety notice

Beryllium and its compounds can cause different diseases like the acute berylliosis, the chronic beryllium disease (CBD), contact dermatitis and cancer. Especially the inhalation of Be containing dust or the contact to solvable Be salts is dangerous. Consequently, the complete handling of starting materials and Be containing samples was carried out in a designated glovebox. Samples outside the glovebox were only transported in closed vessels. For unavoidable work with Be outside the glovebox (e.g. cleaning working equipment) care must be taken to additional safety precautions like FFP3-mask and the avoidance of dusts. Guidelines how to work with Be are available in the literature.^[1-2]

Preparation of starting materials

 Be_3N_2 was synthesized by the reaction of elemental Be (flakes, ABCR, 99+%) in a N_2 atmosphere at 1500 °C for 10 h in a radiofrequency furnace (8TIG 10/100; Hüttinger Elektronik Freiburg, Germany).^[3] Phase purity was confirmed by means of powder X-ray diffraction. Ge_3N_4 (Sigma-Aldrich, >99.99%) was purchased and used at it is.

High-pressure high-temperature synthesis

BeSiN₂ was synthesized in a modified route according to *Eckerlin* in a high-temperature approach, starting from stoichiometric amounts of Be_3N_2 (21.1 mg, 0.384 mmol) and Si_3N_4 (53.9 mg, 0.384 mmol) under N₂ atmosphere.^[4] To prevent oxygen exposure and hydrolysis and because of safety reasons (see above), the starting materials were handled in an Ar-filled glovebox (Unilab, MBraun, Garching; O_2 , $H_2O < 1$ ppm). The starting materials were finely ground and pressed to a thin pill with a diameter of 10 mm. This pill was placed in a tungsten crucible, which was transferred to radiofrequency furnace (8TIG 10/100; Hüttinger Elektronik Freiburg, Germany). The exact synthesizing temperature, described in the literature, stays unclear. Hence, we repeat the synthesis at different temperature steps. It is remarkably, that even at 1700 °C, the starting materials do not react quantitatively. A good crystalline sample with crystals up to 40 μ m was obtained with the following program: The sample was heated up to 1800 °C within 10 min, held at this temperature for 2 h, following heated up to 1900 °C within 10 min, held at this temperature for 8 h and cooled down to 500 °C within 8 h closed by switch off of the furnace and natural cooling. The step at 1800 °C was implemented to start the reaction. By directly heating the sample to 1900 °C, parts of Si₃N₄ starts vaporizing out of the crucible and consequently some Be_3N_2 is left after the reaction.

BeGeN₂ was synthesized in high-temperature high-pressure approach in a hydraulic 1000 t press utilizing the multianvil technique with a modified Walker module.^[5-6] First, a MgO octahedron was prepared as follows: A ZrO₂ cylinder, equipped with two graphite furnaces and MgO spacers was placed in the center of a drilled MgO octahedron (5% Cr₂O₃ doped MgO, 18 mm edge length,

Ceramic Substrates & Components Ltd, Isle of Wight). The graphite furnaces were contacted with Mo plates. Following, stoichiometric amounts of Be_3N_2 (13.4 mg, 0.243 mmol), Ge_3N_4 (66.6 mg, 0.243 mmol) and 2% of NH_4N_3 (1.6 mg, 0.026 mmol) were ground in a tungsten carbide mortar in a glovebox (see above). NH_4N_3 was added to improve the crystallinity of the reaction product. The mixture was packed in h-BN crucible (Henze, Kempten) and transferred in the prepared MgO octahedron. The so filled octahedron was placed in the void of eight tungsten carbide cubes with truncated corners, which were separated with pyrophyllite gaskets. The assembly was transferred to the multianvil apparatus and compressed to 6 GPa within 170 min. At this pressure the sample was heated to 780 °C within 60 min, dwelled at this temperature for 240 min and cooled down to room temperature within 60 min before the pressure was decreased to ambient pressure within 510 min.

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy

For electron microscope investigations, the sample was positioned on a self-adhesive carbon foil and coated with carbon using an electron beam evaporator (BAL-TEC MED 020, BalTec AG, Pfäffikon) to guarantee electrical conductivity. For SEM imaging and EDX measurements a Dualbeam Helios Nanolab G3 UC (FEI, Hilsboro) equipped with an X-Max 80 SDD detector (Oxford instruments, Abingdon) was used. The data was processed with the Aztec software.^[7] The accelerating voltage for SEM imaging and EDX measurements was 5.0 kV.

Solid state magic-angle spinning (MAS) NMR spectroscopy

For solid state NMR measurements the sample was ground and loaded in a ZrO₂ rotor with an outer diameter of 2.5 mm. Tightly packed Teflon tape was used as spacer at the bottom and the top of the rotor to avoid direct contact of the Be-containing sample with the environment. NMR spectra were collected at 10 kHz spinning frequency on an Avance III 500 spectrometer (Bruker, Karlsruhe) with a 11.7 T magnet (500.25 MHz ¹H frequency).

For the evaluation of the measured data, quadrupolar interactions have to be taken into account, since ⁹Be possesses spin *I* = 3/2, leading to quadrupolar broadening of the line shape. Hence, the central transition was fitted with the program DMFIT to analyze the shape of the signal and to elucidate the values for the isotropic chemical shift (δ_{iso}), the quadrupolar coupling constant (C_q).^[8] While the fitting routine also returns the listed values for the asymmetry parameter η_q (Table S10), these should be considered unreliable, since for the relatively small magnitudes of C_q values, the typical features of a second-order broadening line shape (which are essential for determining η_q) are not observable.

All spectra were indirectly referenced to ¹H in 100% tetramethylsilane (TMS) at -0.1240 ppm.

Temperature dependent powder X-ray diffraction (HT-PXRD)

The thermal stability of $BeGeN_2$ and $BeSiN_2$ were examined by temperature-dependent powder Xray diffraction. The ground samples were loaded into silica capillaries (Hilgenberg, Malsfeld) with an outer diameter of 0.5 mm and heated under Ar atmosphere from 50 to 900 °C in steps of 50 °C with a rate of 10 °C/min. After each temperature step during heating and cooling, powder diffraction patterns were collected within 1 h at constant temperature on a STOE Stadi P
diffractometer (STOE & Cie GmbH, Darmstadt, Ag-K α_1 radiation, $\lambda = 0.55942$ Å, Ge(111) monochromator, IP-PSD detector) equipped with a STOE resistance graphite furnace.

Powder X-ray diffraction (PXRD), structure solution and Rietveld refinement

For PXRD measurements the samples were ground and sealed in glass capillaries (0.3 mm outer diameter, Hilgendberg, Malsfeld). After centering the capillary in a rotating goniometer head, data was collected on a STOE Stadi P diffractometer (STOE & Cie GmbH, Darmstadt) in a modified Debye-Scherrer geometry with Cu-K α_1 radiation ($\lambda = 1.54060$ Å) or Ag-K α_1 radiation ($\lambda = 0.55942$ Å) equipped with a MYTHEN 1K strip detector and a Ge(111) monochromator.

For all steps of the structure solution the program package TOPAS Academic was used.^[9] First, the diffraction pattern of BeGeN₂ was compared to known II-IV-N₂ wurtzite type structures. Since it is not related to any of those compounds, the diffraction pattern was indexed and the metric was determined to orthorhombic primitive with the lattice parameters a = 5.1123, b = 4.8360 and c = 2.9815 Å. Following, the diffraction pattern was fitted with a Pawley-Fit to generate the list of hkl indices. Via charge flipping, the starting model for a Rietveld refinement was obtained. During the refinement process, lattice parameter and fractional coordinates for BeGeN₂ were freely refined. The site occupancies were freely refined one after the other. The value for the isotropic thermal expansion was set to a value comparable to those in other beryllium nitrides.^[10] For Ge it was freely refined. No sign for disorder or mixed occupancy was detected. After the Rietveld refinement, the symmetry of the structure was checked with the Platon ADDSYM program,^[11] but the space group *Pmc*2₁ was confirmed.

The Rietveld refinement of BeSiN₂ was carried out on the structural model described by *Eckerlin*, confirming the known model.^[4]

The peak profiles for both refinements were described with the fundamental parameter approach. A potential preferred orientation of the crystallites was accounted for with a 4th order harmonic function and the background was modeled by a shifted Chebyshev polynomial.^[12-13] The results were plotted using Origin.^[14] Structures were visualized using VESTA.^[15]

Raman spectroscopy

Raman measurements were carried out with a custom set-up in Frankfurt described in detail elsewhere.^[16] We used an OXXIUS S.A. Laser-Boxx LMX532 laser (λ = 532 nm) and a spectrograph (Princeton Instruments ACTON SpectraPro 2300i) equipped with a Pixis256E CCD camera. Measurements were performed in reflection geometry with the polarized laser light, where the sample was placed in glass capillary in order to avoid any exposure to air. The results were plotted using Origin.^[14] The theoretic calculated spectra (see DFT calculations) were scaled by factor of 1.0332 for BeGeN₂ and 1.0227 for BeSiN₂.

Second Harmonic generation

Second harmonic generation (SHG) measurements were performed on microcrystalline powder samples with the different grain sizes as a single layer or in filled glass capillary using the Kurtz-Perry approach.^[17] Al₂O₃, KDP (KH₂PO₄) and quartz and were used as reference materials. A Q-

switched Nd:YAG laser (1064 nm, 5-6 ns, 2 kHz) was used for the generation of the fundamental pump wave. The fundamental infrared light was separated using a harmonic separator, a short-pass filter, and an interference filter from the generated second harmonic (532 nm). The generated SHG signal was collected with a photomultiplier and an oscilloscope from five different areas of the sample. On each position, 64 pulses were measured and averaged. Background signals between the laser pulses were used to correct the measured intensities. The SHG measurements were performed under ambient conditions in transmission geometry.

Density functional theory (DFT) calculations

Atomistic model calculations were carried out within the framework of DFT^[18] and the pseudopotential method using the CASTEP simulation package.^[19] Norm-conserving pseudopotentials were generated "on the fly" using the parameters provided with the CASTEP distribution. These pseudopotentials have been extensively tested for accuracy and transferability.^[20] The pseudopotentials were employed in conjunction with plane waves up to a kinetic energy cutoff of 1320 eV. The calculations were carried out with the PBE exchangecorrelation functional.^[21] Monkhorst-Pack grids^[22] were used for Brillouin zone integrations with a distance of < 0.025 Å⁻¹ between grid points. Convergence criteria included an energy change of $< 5 \times 10^{-6}$ eV/atom, a maximal force of < 0.008 eV/Å, and a maximal deviation of the stress tensor < 0.02 GPa from the imposed stress tensor. Optical properties were computed as described by Refson et al.^[23] Phonon frequencies were obtained from density functional perturbation theory (DFPT) calculations. Raman intensities and NLO properties were computed using DFPT with the '2n+1' theorem approach.^[24] The formalism required to obtain space averaged Raman scattering cross section implemented in CASTEP has been presented by Porezag and Pederson.^[25] It should be stressed that all calculations were carried out in the athermal limit, i.e., the influence of temperature and zero-point motion were not taken into account.

The shown ground state energies for BeGeN₂ and BeSiN₂ in the space groups *Pmc*2₁ (No. 26), *Pca*2₁ (No. 29), *Pmn*2₁ (No. 31) and *Pna*2₁ (No. 33) where obtained from periodic DFT linear first principle electron structure calculations via the Vienna *ab initio* simulation package (VASP).^[26-28] Core and valence electrons are separated by projector augmented waves (PAW).^[29-30] Analogue to the atomistic model calculations the generalized gradient approximation (GGA), as described by Perdew, Burke and Ernzerhof (PBE)^[20] was used for the exchange- and correlation-energy. The vdW-dispersion energy-correction as described by Grimme *et al.* was taken into account by the DFT-D3(BJ)^[31] method with Becke-Johnson damping function.^[32] Non-spherical contributions to the gradient of the density in the PAW spheres were included. The structure optimization was performed via conjugate gradient algorithm on a Γ centered (11x6x7) *k*-point grid with an energy cut off of 520 eV to ensure well converged structures and the interpolation of the *k* space was done via the tetrahedron method with Blöchl corrections. The energy convergence criterion was set to 10⁻⁷ eV and the residual atomic forces were relaxed until the convergence criterion of 10⁻⁶ eV/Å was reached.

UV/VIS reflectance spectroscopy

The optical band gap was assessed *via* UV/VIS spectroscopy. Diffuse reflectance spectra were collected at room temperature on a Jasco V-650 UV/VIS spectrophotometer equipped with Czerny–Turner mount, photomultiplier tube detector, deuterium (190–350 nm) and halogen (330–900 nm) lamps as light sources. The measured reflectance spectra were converted to pseudo-absorption spectra using the Kubelka-Munk function ($F(R)=(1-R)^2/2R$).^[33] The results for (F(R)hv)^{1/n} (with n=1/2, assuming a direct band gap) are plotted versus hv in a so-called Tauc-Plot.^[34] The tangent that touches the inflection point indicates the band gap energy (see Figure 8 and S14).

Diamond Anvil Cell setup

For the investigation of the high-pressure behavior of $BeSiN_2$, experiments were carried out in several Boehler-Almax BX90 diamond anvil cells, equipped with pairs of Boehler-Almax-type diamonds with a culet size of 100 or 250 µm, respectively.^[35] The anvils were separated using a Re gasket with a laser-drilled hole of 50 and 130 µm, respectively, forming a cavity. The cells were loaded with single crystals of BeSiN₂. Ne severed as a pressure-transmitting medium and pressure marker. After stepwise compression to the desired pressure under ambient temperature, the particular crystal or sample was heated from both sides using a near-infrared (NIR) fiber laser ($\lambda = 1070$ nm, focused to 20x20 µm²), while with *in situ* X-ray diffraction the reaction process was observed. After heating, XRD data were collected.

Single Crystal X-ray diffraction with Synchrotron radiation

Compression data on single crystals of BeSiN₂ was collected on the synchrotron beamline 13IDD ($\lambda = 0.2952$ Å, Pilatus 1M CdTe detector) at the APS in Chicago, USA and at the beamline ID27 ($\lambda = 0.3344$ Å, Eiger2 X 9m CdTe detector) at ESRF in Grenoble. France. The beam diameters were about 1–3 µm. At each pressure step, single crystal X-ray diffraction data upon rotation of the DAC around the vertical axis of the goniometer ω in a range from –30° to +30° with a scanning step of 0.5° was collected. Ne served as a pressure marker: Via the equation of state of Ne combined with the unit cell volume of Ne elucidated with a LeBail-Fit, the pressure was accurately determined at each pressure point.^[36]

The diffraction data was processed with the CrysAlisPro software.^[37] To calibrate the instrument model, a single-crystal of ortho-enstatite ($(Mg_{1.93}, Fe_{0.06})(Si_{1.93}, Al_{0.06})O_6$, a = 8.8117(2), b = 5.18320(10), c = 18.2391(3) Å) was used. Structure solution and refinement was carried out with SHELXS and SHELXT in program package WinGX.^[38-40]

Equation of State

Using the pressure-volume data from pressure-dependent single crystal refinement of $BeSiN_2$ from ambient pressure to 90 GPa, the reduction of the unit cell volume was fitted by a 3rd order Birch-Murnaghan equation of state (Equation 3.1) with the program package EoSFit7.^[41-43]

$$p(V) = \frac{3}{2} K_0 \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \cdot \left[1 + \frac{3}{4} (K_0' - 4) \left\{ \left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right\} \right]$$
(3.1)

(K₀: isothermal bulk modulus, V₀: unit cell volume at a theoretical pressure of 0, V: unit cell volume, K₀' partial pressure derivative of the isothermal bulk modulus)

Results and Discussion



SEM images and EDX measurements

Figure S3.1. SEM images of polycrystalline BeGeN₂ (a, b) and BeSiN₂ (c, d). Crystallites of BeGeN₂ are up to 5 μ m in length and 2 μ m in width. Crystals of BeSiN₂ (c, d) are much bigger with up to 40 μ m in length. This difference may arise from the different synthesis methods (see above).

EDX measurements were carried out on different crystallites of $BeGeN_2$ (table S1) and $BeSiN_2$ (table S2). For $BeGeN_2$ no other elements than Ge, N and O were detected. Be is very difficult to detect next to heavier elements like Ge via EDX spectroscopy. The content of O can be attributed to surface hydrolysis, due to the harsh washing conditions with 30% H_2O_2 in concentrated NaOH to remove elemental Ge. For $BeSiN_2$ no other elements than Be, Si, N and O were detected. The content of O determined for $BeSiN_2$ is far lower than for $BeGeN_2$, since it was not washed before the analysis. For both compounds, the normalized ratio is in very good agreement to the theoretical values, considering the precision of the method for light elements.

Measurement	Ge	Ν	0
1	30	50	19
2	37	60	3
3	28	62	11
4	31	58	10
5	37	47	15
Average	33(4)	55(6)	12(4)
Normalized	1.0(1)	1.7(1)	0.4(1)
Theoretical	1	2	0

Table S3.1. EDX measurements of $BeGeN_2$. Results are given in atomic percent with standard deviations in parenthesis.

Table S3.2. EDX measurements of $BeSiN_2$. Results are given in atomic percent with standard deviations in parenthesis.

Measurement	Ве	Si	Ν	0
1	27	26	46	1
2	28	28	43	1
3	31	29	39	1
4	29	30	40	1
5	27	30	42	1
Average	28(1)	29(1)	42(2)	1(0)
Normalized	1.0(1)	1.0(1)	1.5(1)	0.1(1)
Theoretical	1	1	2	0

Structure determination and Rietveld refinement



Figure S3.2. Result of the Rietveld refinement of BeSiN₂. Observed (black crosses), calculated (red line) powder X-ray diffraction patterns (AgK α_1 , λ = 0.55942 Å) and difference plot (gray line). Positions of Bragg reflections of BeSiN₂ and W are given as black and blue bars, respectively. The small amount of W (< 1%) can be accounted to the scraping of the W crucible.



Figure S3.3. Result of the Rietveld refinement of BeGeN₂. Observed (black crosses), calculated (red line) powder X-ray diffraction patterns (AgK α_1 , λ = 0.55942 Å) and difference plot (gray line). Positions of Bragg reflections of BeGeN₂ are given as blue bars.

Formula	BeGeN ₂
Crystal system	orthorhombic
Space group	<i>Pmc</i> 2 ₁ (no. 26)
Lattice parameters / Å	a = 2.97976(10)
	<i>b</i> = 5.11452(18)
	<i>c</i> = 4.83496(19)
Cell volume /Å ³	73.685(5)
Formula units per unit cell	2
Density / g cm ⁻³	4.951
Molecular weight / g mol ⁻¹	109.64
Diffractometer	Stoe Stadi P
Radiation	Ag-Kα1 (λ = 0.55942 Å)
Detector	Mythen 1K
Monochromator	Ge(111)
2θ range / °	$1.0 < 2\theta < 40.180$
Step width / °	0.015
Data points	2613
Total number of reflections	96
refined parameters	32
Background function	Shifted Chebyshev
Number of background parameters	12
Goodness of fit	2.327
$R_p; R_{wp}$	0.037; 0.047
R _{exp} ; R _{bragg}	0.020; 0.017

 $\label{eq:stable} \textbf{Table S3.3.} Crystallographic data of BeGeN_2 from Rietveld refinement. Standard deviations are given in parenthesis.$

Table S3.4. Wyckoff positions, coordinates, isotropic thermal displacement parameters and occupancy of BeGeN₂. Standard deviations are given in parenthesis.

Atom	Wyck.	x	у	Ζ	U _{eq} / Å	Occ.
Be1	2 <i>b</i>	1/2	0.324(5)	0.11(6)	0.009	1
N1	2 <i>b</i>	1/2	0.352(4)	0.478(4)	0.009	1
Ge1	2 <i>a</i>	0	0.1736(4)	0.612(4)	0.006	1
N2	2a	0	0.185(3)	0	0.009	1

Atom1 - Atom2	Distance / Å	Atom1 - Atom2	Distance / Å
Be1 – N1	1.77853(7)	Ge1-N1	1.86326(5)
Be1 – N1	1.77883(6)	Ge1 – N1	1.86326(5)
Be1 – N2	1.73583(5)	Ge1 – N2	1.87379(8)
Be1 – N2	1.73583(5)	Ge1 – N2	1.91648(7)

 $\label{eq:stable} \textbf{Table S3.5.} Interatomic distances in BeGeN_2 from Rietveld refinement. Standard deviations are given in parenthesis.$

Table S3.6. Interatomic angles of $BeGeN_2$ from Rietveld refinement. Standard deviations are given in parenthesis.

Atoms	Angle / °	Atoms	Angle / °	Atoms	Angle / °
N1 – Ge1 – N1	106.186(3)	N1 – Be1 – N1	106.5746(13)	Be1 – N1 – Be1	115.9371(8)
N1 – Ge1 – N2	109.3222(10)	N1 – Be1 – N2	110.1710(8)	Be1 – N2 – Be1	118.255(3)
N1 – Ge1 – N2	109.3222(10)	N1 – Be1 – N2	110.1710(8)	Be1 – N1 – Ge1	107.8197(10)
N1 – Ge1 – N2	111.7844(14)	N1 – Be1 – N2	105.4172(13)	Be1 – N2 – Ge1	109.0178(9)
N1 – Ge1 – N2	111.7844(14)	N1 – Be1 – N2	105.4172(13)	Ge1 – N1 – Ge1	106.186(3)
N2 – Ge1 – N2	108.3956(8)	N2 – Be1 – N2	118.255(3)		

Comparison of the space groups Pmc21, Pmn21, Pna21 and Pca21



Figure S3.4. The four possible arrangements for a wurtzite-type structure in 1:1:2 stoichiometry, depicted by the space groups *Pmc*2₁ (top left), *Pmn*2₁ (top right), *Pna*2₁ (bottom left) and *Pca*2₁ (bottom right) on the example of BeGeN₂. BeN4 and GeN4 tetrahedra are illustrated in green and blue, respectively. Nitrogen occupies the tetrahedra corners and is not depicted.

The difference between the space groups in the two columns (first column: no. 26 and 33; second column: no. 31 and 29) becomes clear, focusing on the tetrahedral corners: In the left column, each corner is connected to two green and two blue tetrahedra. On the right it is three tetrahedra of one color. Within the column, the difference lies in the formation of rows of tetrahedra in one color in space groups no. 26 and 31, while for space groups 33 and 29 the tetrahedra alternate. The two arrangements in space groups no. 29 and 31 break the octet rule of local charge neutrality. One nitrogen atom is bound to three group II atoms and one group IV atom or vice versa. This is not the case for the octet rule obeying arrangements in space groups 26 and 33 in which one nitrogen atom is surrounded by two cations of group II and group IV.

The relationship between those space groups can be described via a Bärnighausen tree, that was already made for wurtzite-related compounds by *Breternitz et al.*.^[44] More detailed information about symmetry relations in wurtzite-type structures is available in the literature.^[45-46]

Comparison of ionic radii

Table S3.7. Selection of possible cations building wurtzite type structures in a $II-IV-N_2$ formula type and their ratio.^[47] Only BeGeN₂ exhibits a ratio smaller one. The symbol # means, that a wurtzite-type compound with this elements does not exist, so far.

M ²⁺	radius / Å	M^{4+}	radius / Å	ratio	literature
	0.27	Si ⁴⁺	0.26	1.038	[4]
Be ²⁺	0.27	Ge ⁴⁺	0.39	0.692	this work
	0.27	Sn ⁴⁺	0.55	0.491	#
	0.57	Si ⁴⁺	0.26	2.192	[48]
Mg ²⁺	0.57	Ge ⁴⁺	0.39	1.462	[48]
	0.57	Sn ⁴⁺	0.55	1.036	#
	0.60	Si ⁴⁺	0.26	2.308	[49]
Zn ²⁺	0.60	Ge ⁴⁺	0.39	1.538	[50]
	0.60	Sn ⁴⁺	0.55	1.091	[51-52]
	0.66	Si ⁴⁺	0.26	2.538	[53]
Mn ²⁺	0.66	Ge ⁴⁺	0.39	1.692	[53]
	0.66	Sn ⁴⁺	0.55	1.200	#
	0.63	Si ⁴⁺	0.26	2.423	#
Fe ²⁺	0.63	Ge ⁴⁺	0.39	1.615	#
	0.63	Sn ⁴⁺	0.55	1.145	#
	0.58	Si ⁴⁺	0.26	2.231	#
Co ²⁺	0.58	Ge ⁴⁺	0.39	1.487	#
	0.58	Sn ⁴⁺	0.55	1.055	#
	0.55	Si ⁴⁺	0.26	2.115	#
Ni ²⁺	0.55	Ge ⁴⁺	0.39	1.410	#
	0.55	Sn ⁴⁺	0.55	1.000	#

Charge distribution (CHARDI)

Table S3.8: Results of the CHARDI analysis for BeGeN₂. All effective coordination numbers and the mean total charges are in good agreement with the theoretical values.

Tetrahedron	Be N1 N1 N2 N2	Ge N1 N1 N2 N2
Average bong length / Å	1.7573	1.8792
Polyhedral volume / ų	2.7615	3.3985
Distortion index (bond length)	0.01219	0.00992
Quadratic elongation	1.0058	1.0015
Bond angle variance / ° ²	23.8783	4.5397
Effective coordination number (theory)	3.9788 (4)	3.9814 (4)
Total charge (theory)		
Be / Ge	2.002 (2.000)	3.998 (4.000)
N1	-3.028 (-3)	-3.028 (-3)
N2	-2.972 (-3)	-2.972 (-3)

MAPLE

Table S3.9: Results of MAPLE calculations show a difference of 0.4% in the Madelung part of lattice energy for BeGeN₂ compared to the sum of the respective binary nitrides Ge_3N_4 and Be_3N_2 .

	$Be_3N_2 + Ge_3N_4$	\rightarrow	3 BeGeN ₂	
Ge ₃ N ₄	50368 kJ/mol	BeGeN ₂	3 x 23333 kJ/mol	
α -Be ₃ N ₂	19876 kJ/mol			
	70244 kJ / mol		69999 kJ / mol	0.4% difference

Solid state MAS NMR spectroscopy



Figure S3.5: Solid state MAS NMR spectra of ⁹Be of BeGeN₂ (a, b) and BeSiN₂ (c, d) each at a spinning frequency of 10 kHz. Spinning side-bands are marked with asterisks. a) ⁹Be spectrum of BeGeN₂ shows a single resonance. The spectrum shows no other Be signal. b) Fit of the spectrum shown in a) to determine the chemical shift δ_{iso} and the magnitude of the quadrupolar interaction.c) ⁹Be spectrum of BeSiN₂ with one Be signal. d) Fit of the spectrum shown in c) to obtain values for the isotropic chemical shift δ_{iso} and for the magnitude of the quadrupolar interaction.

	BeGeN ₂	BeSiN₂	$Be_{3}N_{2}^{[54]}$
position / ppm	4.6	3.5	2.2
$\delta_{ ext{iso}}$ / ppm	6.1	5.5	3.5
C _Q / MHz	0.49	0.57	0.55
$\eta_{ m Q}$	0.83	0.72	0.87

Table S3.10. Fit results for the NMR spectra of BeGeN₂ and BeSiN₂ and their comparison to Be₃N₂.

Second harmonic generation (SHG)

Table S3.11.	Results o	f SHG	measureme	ents on	powder	samples	of quartz	, KDP	(KH ₂ PO ₄),	Al ₂ O ₃ ,	BeGeN ₂
BeSiN ₂ .											

Samples	SHG intensities in mV					
Samples	One layer	In capillary				
Quartz (<5 µm)	29(10)					
Quartz (5–25 µm)	238 (28)	20(14)				
Quartz (25–50 μm)	380 (81)	24(11)				
Al₂O₃ (9 μm)	0 (1)	0(1)				
KDP (5–25 μm)	730 (38)	41(17)				
KDP (25–50 μm)	1932 (367)	172(32)				
BeGeN₂ (<2 μm)		29(4)				
BeSiN ₂ (5–60 μm)		23(7)				

Both title compounds show weak SHG signals. However, the calculated SHG tensor coefficients ($d_{15} = 2.4 \text{ pm/V}$, $d_{24} = 2.9 \text{ pm/V}$ and $d_{33} = -5.0 \text{ pm/V}$) of BeGeN₂ with the space group *Pmc*2₁ are much larger than the tensor coefficients of quartz ($d_{11} = 0.3 \text{ pm/V}$). This disagreement between experiment and calculation may be explained by large difference between the grain sizes of the BeGeN₂ powder sample and the reference quartz sample. The combination of the low SHG intensity and high calculated values is indicative of a non phase-matching condition. On the other hand, the calculated SHG tensor coefficients of BeSiN₂ with the space group *Pna2*₁ are $d_{15} = -1.5 \text{ pm/V}$, $d_{24} = -1.4 \text{ pm/V}$ and $d_{33} = -0.36 \text{ pm/V}$, where the crystals of BeSiN₂ have similar grain sizes to the reference. Therefore, a determination of phase-matching conditions and an explanation about the disagreement between experiment and calculation require further investigations.

DFT calculations

space group	energy differe	energy difference / eV f.u. ⁻¹			
space group	BeSiN ₂	BeGeN ₂			
Pmc2 ₁	0.020	-			
Pna21	-	0.018			
Pca21	0.910	0.847			
Pmn2 ₁	1.069	1.044			

Table S3.12. Energy differences between the ground state and the structure in the respective space group in eV per formula unit (f.u.)



Figure S3.6. Results of DFT calculations (Table S12) of BeSiN₂ and BeGeN₂ for all four possible ordered wurtzite-type structures, represented by their space groups.

HT-PXRD



Figure S3.7: Temperature dependent powder X-ray diffraction pattern (Ag-K α_1 radiation, $\lambda = 0.55942$ Å) of BeGeN₂ measured under Ar atmosphere up to 900 °C. No significant change in the unit cell can be observed. At 750 °C the decomposition in Ge starts.



Figure S3.8: Temperature-dependent evolution of the cell volume and the lattice parameters of BeGeN₂ with linear fits. ($\alpha_a = 5.9(1)$; $\alpha_b = 6.6(1)$; $\alpha_c = 5.6(1)$; $\alpha_V = 18.1(3)$ ppm K⁻¹).



Figure S3.9. Temperature dependent powder X-ray diffraction pattern (Ag-K α_1 radiation, $\lambda = 0.55942$ Å) of BeSiN₂ measured under Ar atmosphere up to 900 °C. No significant change in the unit cell can be observed.



Figure S3.10. Temperature-dependent evolution of the cell volume and the lattice parameters of BeSiN₂ with linear fits. ($\alpha_a = 5.9(2)$; $\alpha_b = 6.9(2)$; $\alpha_c = 6.1(2)$; $\alpha_v = 18.8(5)$ ppm K⁻¹).

Diamond Anvil Cell experiments with BeSiN₂

For high-pressure high-temperature experiments in a Diamond Anvil Cell we have prepared two cells as described above. The following list of performed experiences is given for the sake of completeness and to pass on our experiences with BeSiN₂ (see Table S13). The first cell with single crystals (sc) of BeSiN₂ was compressed to 40 GPa and was laser heated online while *in situ* X-ray diffraction experiments gave insights, if BeSiN₂ undergoes a phase transition. No reaction up to 3500 K was detected. The second cell was compressed up to 90 GPa and heated it in the range of 2000 up to 7800 K. At this point, BeSiN₂ was ablated, no reaction or phase transition before or at this temperature point was observed (see figure S12). Summarized, we have not detected any phase transition to BeGeN₂-type BeSiN₂ or any other phase transition as stated in the literature,^[55] but could reveal ultra-incompressible behavior of BeSiN₂ from pressure-volume data. (K = 374(5) GPa, K' = 1.53(10), see figure S13).

DAC number	starting materials	max. <i>p</i> / GPa	max. <i>T</i> / K	products
1	BeSiN ₂ - sc	40	3500	BeSiN ₂
2	BeSiN ₂ - sc	90	7800	ablation

Table S3.13. List of DAC experiments examining the high-pressure behavior of BeSiN₂



Figure S3.11. Picture of the cavity of a DAC at 90 GPa with a tungsten peace, two single crystals of $BeSiN_2$ and a piece of ruby, before heating to the maximum temperature of 7800 K (left) and after heating (right). The partially decomposition of the upper crystal is clearly visible. However, the remaining part is still $BeSiN_2$.



Figure S3.12. Pressure-volume data from pressure-dependent single crystal refinements of $BeSiN_2$ fitted with a 2nd and 3rd order Birch-Murnaghan equation of state (BM EoS,). The fit for the 2nd order describes the data worse than the fit for the 3rd order.

Discussion of the elastic properties of BeSiN₂

The pressure-volume data was initially fitted using a 2nd order Birch-Murnaghan equation of state (Figure S13) with the fitting parameters $V_0 = 133.84(5)$ Å³, $K_0 = 283(7)$ GPa and $K_0' = 4.0$ (fixed). However, a significant discrepancy can be observed between the fit and the experimental data over the entire pressure scale. Therefore, we have repeated the fit with a 3rd order Birch-Murnaghan equation of state with fitting parameters $V_0 = 133.84(5)$ Å³, $K_0 = 374(5)$ GPa and $K_0' = 1.53(10)$, which fits the experimental data very well. For both fits, the unit cell volume at ambient pressure (V_0) was fixed, as we determined it with SCXRD at ambient pressure.

The determined bulk modulus $K_0(BeSiN_2) = 374(5)$ GPa appears to be higher than previously proposed by DFT calculations ($K_{0,calc} = 220-263$ GPa).^[55-56] One reason for this significant deviation could arise from errors in the experimental data, for example non-hydrostatic conditions inside the DAC. However, we determined the pressure by the equation of state of Ne, whose Bragg peaks measured exactly at the same point as the SCXRD data sets of BeSiN₂. Where possible, for example when a map of the entire cavity was taken, we double-checked the pressure by Au and Re. A second reason can be found in the uncertainty of DFT calculations for the elastic properties as demonstrated in the literature.^[57] BeSiN₂ could also have a more covalent character than assumed in theoretical studies, since the covalency can be correlated with the elastic properties of a compound.^[58] This effect is known from other, ultra-incompressible beryllium nitrides like sp-BeP₂N₄ ($K_{0,calc} = 268-291$ GPa; $K_{0,exp} = 325(8)$ GPa).^[59] Another reason could be the presence of

defects in the selected single crystals of $BeSiN_2$. One indication for this is the presence of Urbach tails in the Tauc plot (Figure S14).

A systematic investigation of the bulk modulus of wurtzite-type compounds, e.g. the row of $MSiN_2$ (M = Be, Mg, Zn), could reveal the influence of the covalency of the M–N bond on the incompressibility of a material. *Riedel et al.* have already investigated MgSiN₂ under high-pressure high-temperature conditions, revealing the structure of β -MgSiN₂ in the α -NaFeO₂ structure type. However, no examination of the elastic properties were conducted in this work.^[60]

UVVIS measurements





The evaluated band gap energies of BeSiN₂ and BeGeN₂ deviate from the expected trend of decreasing band gap energies towards the heavier homologue. One reason for this could be the presence of defects as known for wurtzite-type structures. An indication of this is the presence of Urbach tails in the Tauc plot.^[61] XAS and XES measurements on well-tempered samples could determine the band gap energies more precisely and could reveal whether the difference arises from defects or from the different structures.

	band gap / eV		
method	BeSiN ₂	BeGeN ₂	
LDA ^[62]	5.1	5.2	
LDA ^[56]	4.9	3.7	
GW GGA ^[63]	7.7	5.0	
experiment	4.5	4.9	

Table S3.14. Comparison o	f experimental	assessed band ga	ap energies with	those from the	literature. ^[56, 62-63]
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8.3 Supporting Information for Chapter 4

Experimental Procedures

Safety notice

Beryllium and its compounds can cause different diseases like the acute berylliosis, the chronic beryllium disease (CBD), contact dermatitis and cancer. Especially the inhalation of Be containing dust or the contact to solvable Be salts is dangerous. Consequently, the complete handling of starting materials and Be containing samples was carried out in a designated glovebox. Samples outside the glovebox were only transported in closed vessels. For unavoidable work with Be outside the glovebox (e.g. cleaning working equipment) care must be taken to additional safety precautions like FFP3-mask and the avoidance of dusts. Guidelines how to work with Be are available in the literature.^[1-2]

Preparation of starting materials

 Be_3N_2 was synthesized by the reaction of elemental Be (flakes, ABCR, 99+%) in a N_2 atmosphere at 1500 °C for 10 h in a radiofrequency furnace (8TIG 10/100; Hüttinger Elektronik Freiburg, Germany).^[3] Phase purity was confirmed by means of powder X-ray diffraction.

NH₄N₃ was synthesized according to *Frierson* by a metathesis reaction between NH₄NO₃ (Grüssing, 99%) and NaN₃ (Acros Organics, 99%) in a Schlenk tube in a furnace at 170 °C. NH₄N₃ vaporizes at this temperature and recrystallizes at the cold Schlenk cap, which is positioned outside the furnace. A more detailed description of the NH₄N₃ synthesis can be found in the literature.^[4] W (Goodfellow, 99.9%) was purchased and used as it is.

High-pressure high-temperature synthesis

 $W_2Be_4N_5$ was synthesized in high-temperature high-pressure approach in a hydraulic 1000 t press utilizing the multianvil technique with a modified Walker module.^[5-6] First, a MgO octahedron was prepared as follows: A ZrO₂ cylinder, equipped with two graphite furnaces and MgO spacers was placed in the center of a drilled MgO octahedron (5% Cr₂O₃ doped MgO, 18 mm edge length, Ceramic Substrates & Components Ltd, Isle of Wight). The graphite furnaces were contacted with Mo plates. Following, stoichiometric amounts of Be₃N₂ (17.0 mg, 0.310 mmol), W (85.4 mg, 0.464 mmol) and NH₄N₃ (13.9 mg, 0.232 mmol) were ground in a tungsten carbide mortar in a glovebox (see above). NaN₃ can be used as a nitrogen source as well. The mixture was packed in a *h*-BN crucible (Henze, Kempten) and transferred in the prepared MgO octahedron. The so filled octahedron was placed in the void of eight tungsten carbide cubes with truncated corners, which were separated with pyrophyllite gaskets. The assembly was transferred to the multianvil apparatus and compressed to 8 GPa within 240 min. At this pressure the sample was heated to 1350 °C within 35 min, dwelled at this temperature for 15 min and cooled down to room temperature within 15 min before the pressure was decreased to ambient pressure within 720 min. W_2N_3 was synthesized according to *Wang et al.* from stoichiometric amounts of Na_2WO_4 (Merck, 99%) and *h*-BN (abcr, 99%) at 5 GPa and 1200 °C.^[7] The starting materials were prepared as described above and heated to 1200 °C within 35 min, dwelled at this temperature for 20 min and finally cooled to room temperature within 15 min. The sample was washed to remove $NaBO_2$, afterwards dried at 120 °C and assesses by PXRD.

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy

For electron microscope investigations, the sample was positioned on a self-adhesive carbon foil and coated with carbon using an electron beam evaporator (BAL-TEC MED 020, BalTec AG, Pfäffikon) to guarantee electrical conductivity. For SEM imaging and EDX measurements a Dualbeam Helios Nanolab G3 UC (FEI, Hilsboro) equipped with an X-Max 80 SDD detector (Oxford instruments, Abingdon) was used. The data was processed with the Aztec software.^[8] The accelerating voltage for SEM imaging and EDX measurements was 20.0 kV.

Inductively coupled plasma optical emission spectrometry (ICP-OES)

Elemental analysis was conducted at a Varian Vista RL with a 40 MHz RF generator, and a VistaChip CCD detector. A washed sample of $W_2Be_4N_5$ was dissolved in a mixture of *aquia regia* and HF. The use of HF is essential. Otherwise, poorly soluble tungsten oxide species falsify the result.

Single crystal X-Ray diffraction (sc-XRD)

Structure determination was carried out by means of single crystal X-ray diffraction (sc-XRD). Data was collected on a Bruker D8 Venture TXS diffractometer with Mo-K α_1 radiation (λ = 0.71073 Å), rotating anode and multilayer monochromator. Indexing, integration, absorption correction (multi-scan) and the determination of the space group was carried out in the APEX3 software package.^[9] The dataset was solved by SHELXT.^[10] The structural model was refined by SHELXL with the least-square method.^[11] Structures were visualized using VESTA.^[12]

Powder X-ray diffraction (PXRD) and Rietveld refinement

For PXRD measurements the samples were ground and sealed in glass capillaries (0.4 mm outer diameter, Hilgendberg, Malsfeld). After centering the capillary in a rotating goniometer head, data was collected on a STOE Stadi P diffractometer (STOE & Cie GmbH, Darmstadt) in a modified Debye-Scherrer geometry with Ag-K α_1 radiation (λ = 0.55942 Å) equipped with a MYTHEN 1K strip detector and a Ge(111) monochromator.

To demonstrate the phase purity of the examined $W_2Be_4N_5$ sample, a Rietveld refinement with the program package TOPAS Academic was carried out.^[13-14] During the refinement process, lattice parameter, fractional coordinates and the site occupancy for $W_2Be_4N_5$ were freely refined. The deviation from the structural model obtained from sc-XRD was within the error limits. The peak profiles were described with the fundamental parameter approach. A potentially preferred orientation of the crystallites was accounted for with a 4th order harmonic function and the background was modeled by a shifted Chebyshev polynomial.^[15-16] The results were plotted using Origin.^[17]

Temperature dependent powder X-ray diffraction (HT-PXRD)

The thermal stability of $W_2Be_4N_5$ was examined by temperature-dependent powder X-ray diffraction. The ground sample was loaded into a silica capillary (Hilgenberg, Malsfeld) with an outer diameter of 0.3 mm and heated under Ar atmosphere from 50 to 900 °C in steps of 50 °C with a rate of 10 °C/min. After each temperature step during heating and cooling, powder diffraction patterns were collected within 1 h at constant temperature on a STOE Stadi P diffractometer (STOE & Cie GmbH, Darmstadt, Ag-K α_1 radiation, $\lambda = 0.55942$ Å, Ge(111) monochromator, IP-PSD detector) equipped with a STOE resistance graphite furnace.

Solid State magic-angle spinning (MAS) NMR spectroscopy

For solid state MAS NMR measurements the sample was ground and loaded in a ZrO_2 rotor with an outer diameter of 2.5 mm. Tightly packed Teflon tape was used as spacer at the bottom and the top of the rotor to avoid direct contact of the Be-containing sample with the environment. The ⁹Be NMR spectrum was collected at 12 kHz spinning frequency on an Avance III 500 spectrometer (Bruker, Karlsruhe) with a 11.7 T magnet (500.25 MHz ¹H frequency).

The spectrum was indirectly referenced to ¹H in 100% tetramethylsilane (TMS) at -0.1240 ppm.

UV/VIS reflectance spectroscopy

The optical band gap was assessed via UV/VIS spectroscopy. Diffuse reflectance spectra were collected at room temperature on a Jasco V-650 UV/VIS spectrophotometer equipped with Czerny–Turner mount, photomultiplier tube detector, deuterium (190–350 nm) and halogen (330–900 nm) lamps as light sources. The measured reflectance spectra were converted to pseudo-absorption spectra using the Kubelka-Munk function $(F(R)=(1-R)^2/2R)$.^[18] The results for $(F(R)hv)^{1/n}$ (with n=1/2, assuming a direct band gap) are plotted versus hv in a so-called Tauc-Plot.^[19] The tangent that touches the inflection point indicates the band gap energy.

Fourier transformed infrared spectroscopy (FTIR)

An infrared spectrum of the sample was collected on a Bruker Alpha II FTIR spectrometer using a diamond attenuated total reflectance (ATR) unit. The spectrum was recorded in a glovebox in the range of 250–4000 cm⁻¹ and with a resolution of 2 cm⁻¹.

Vibrating sample magnetometer

Magnetization measurements were performed on a Physical Property Measurement System (PPMS-9, Quantum Design) using the vibrating sample magnetometer (VSM) option with the Quantum Design MultiVu software.^[20] Isothermal magnetization measurements were performed at 300 and 2 K with a variable field *H* of \pm 50 kOe. Samples were prepared in Quantum Design polypropylene capsules. The diamagnetic contribution of the capsule was corrected for in the acquired data.

Results and Discussion

Images and elemental analysis







EDX measurements were carried out on different crystallites of $W_2Be_4N_5$. No other elements than W, N and O were detected. The latter is probably due to surface hydrolysis. For the unambiguous exclusion of oxygen in the structure of $W_2Be_4N_5$, neutron diffraction would be a suitable technique due to the different scattering lengths of N and O.

Be cannot be detected by means of EDX next to W. Hence, for the precise determination of the Be:W ratio, ICP measurement were conducted. A sample of washed $W_2Be_4N_5$ was solved in a mixture of *aqua regia* and HF. The ratio of Be:W was measured by means of a double termination and is in line with theoretical value (exp.: 1.9:1; theor.: 2:1).

Comparison of the two structural models of $W_2Be_4N_5$



Figure S4.2. Structural model in space group $R\overline{3}m$ (W₂Be₄N₅, left) and space group R3m (W₂Be₃N₅, right). Both structural models occur during the structure solution process. They mainly differ in the kind of condensation of the separating Be–N layers: While in the left model edge-sharing occurs, the right model exhibits only vertex-sharing.

The two models, depicted in Figure S2 occur during the structure solution process and both make sense from a chemical point of view. The stacking order for both models is identical and they mainly differ in the separating Be–N layers (edge- vs. vertex-sharing). However, we favored the centrosymmetric model for the following reasons: First, the chemical analysis (ICP-OES) corresponds to the ratio of Be:W as it is present in W₂Be₄N₅ ($R\bar{3}m$). Second, the quality factors are better with simultaneously less refined parameter in the sc-XRD refinement. Third, the anisotropic refinement of the N atoms is only stable for the model in space group $R\bar{3}m$. Last, but not least, the symmetry descent from $R\bar{3}m$ to R3m results in two different tungsten sites. However, the correlation matrix of the two W atoms indicates strongly, that it is only one crystallographic W atom.

Rietveld refinements and crystallographic information



Figure S4.3. Result of the Rietveld refinement of $W_2Be_4N_5$. Observed (black crosses), calculated (red line) powder X-ray diffraction patterns (AgK α_1 , $\lambda = 0.55942$ Å) and difference plot (gray line). Positions of Bragg reflections of $W_2Be_4N_5$ and diluting BN are given as black and blue bars, respectively. An unaccounted Bragg peak is marked with an asterisk. For the explanation of "o" see below.



Figure S4.4. Result of the Rietveld refinement of $W_2Be_4N_5$ and $W_4Be_8N_9$. Observed (black crosses), calculated (red line) powder X-ray diffraction patterns (AgK α_1 , $\lambda = 0.55942$ Å) and difference plot (gray line). Positions of Bragg reflections of $W_2Be_4N_5$ and $W_4Be_8N_9$ are given as blue bars. For the explanation of "o" see below.

Figure S3 shows the almost phase pure synthesis of $W_2Be_4N_5$. However, additional reflections are visible in the range of $2\theta = 5-7^{\circ}$ (marked with an "o"). They are likely to originate from the stacking reflections of further phases in the Be-W-N system. In the sample, from which we isolated a crystal of $W_4Be_8N_9$ we obtained another crystal with a *c*-axis length of 134.53(2) Å (a = 2.8611(4) Å). However, due to the poor crystal and thus data quality, it was not possible to elucidate the structure. Comparing the crystal structures of $W_2Be_4N_5$ and $W_4Be_8N_9$ (Figure S7), it becomes apparent that there should exist at least one additional compound which consists only of the sublayer "a" of $W_2Be_4N_5$.

Both structures crystallize in the form of plate-like crystals. Dilution is therefore necessary for a Rietveld refinement. However, there are still some reflections visible in the difference plot. These reflections are the stacking reflection (00l). A complete statistical orientation of the crystallites was not possible due to the sample preparation in a capillary. For the Rietveld refinement shown in Figure S4, the sample was not diluted in order to minimize the number of reflections in this phase mixture. Thus, the maxima in the difference plot for the stacking reflections are more intense.

Formula	W ₂ Be ₄ N ₅
Crystal system	trigonal
Space group	<i>R</i> 3 <i>m</i> (no. 166)
Lattice parameters / Å	a = 2.8687(1)
	<i>c</i> = 37.0753(13)
Cell volume /ų	264.23(2)
Formula units per unit cell	3
Density / g cm ⁻³	8.932
Molecular weight / g mol ⁻¹	473.79
Linear absorption coefficient / mm ⁻¹	65.072
T_{\min}/T_{\max}	0.7843
Diffractometer	D8 Venture
Radiation	Mo-Kα ₁ (λ = 0.71973 Å)
Absorption correction	multi-scan
BASF	0.678(3)
F(000)	597
θ range / °	$3.297 \le \theta \le 36.043$
Total no. of reflections	1343
Independent reflections $[l \ge 2\sigma(l)/all]$	208/215
R _{int}	0.030
Refined parameters	17
Goodness of fit	1.206
<i>R</i> -values $[l \ge 2\sigma(l)]$	$R_1 = 0.0277; wR2 = 0.0654$
R-values [all data]	$R_1 = 0.0289; wR2 = 0.0660$
$\Delta ho_{ m max}$, $\Delta ho_{ m min}$ / e Å ³	4.72; –4.02

Table S4.1. Crystallographic data of $W_2Be_4N_5$, refined as an obverse/reverse twin. Standard deviations are given in parenthesis.

Atom	Wyck.	x	у	Z	U _{eq} / Ų	Occ.
W1	6 <i>c</i>	0	0	0.06795(2)	0.0046(1)	1
N1	6 <i>c</i>	0	0	0.2307(3)	0.0063(19)	1
N2	3 <i>c</i>	0	0	1/2	0.007(2)	1
N3	6 <i>c</i>	0	0	0.3007(3)	0.0060(16)	1
Be1	6 <i>c</i>	0	0	0.3420(7)	0.024(5)	1
Be2	6 <i>c</i>	0	0	0.1858(9)	0.031(6)	1

Table S4.2. Wyckoff positions, coordinates, isotropic thermal displacement parameters and occupancy of $W_2Be_4N_5$. Standard deviations are given in parenthesis.

Table S4.3. Anisotropic displacement parameters for W and N in $W_2Be_4N_5$. Standard deviations are given in parenthesis.

Atom	U ₁₁ /Å ²	U ₂₂ / Ų	U ₃₃ / Ų	U ₁₂ / Å ²	U ₁₃ / Ų	U ₂₃ / Ų
W1	0.0020(2)	0.0020(2)	0.0098(2)	0.00098(9)	0	0
N1	0.004(3)	0.004(3)	0.011(4)	0.0021(13)	0	0
N2	0.006(3)	0.006(3)	0.008(6)	0.0028(17)	0	0
N3	0.008(2)	0.008(2)	0.002(4)	0.0040(12)	0	0

Charge distribution (CHARDI)

Table S4.4: Results of the CHARDI analysis for $W_2Be_4N_5$.

Polyhedron	W N1 N1 N1 N3 N3 N3	Be1 N3 N3 N3 N3	Be2 N1 N2 N2 N2
Average bong length / Å	2.1041	1.7925	1.7675
Polyhedral volume / Å ³	9.2481	2.8743	2.8199
Distortion index (bond length)	0.00344	0.07288	0.02908
Quadratic elongation	-	1.0260	1.0044
Bond angle variance / ° ²	-	105.7159	17.6694
Effective coordination number	5.9976	1.8929	3.7700
Total charge (theory)			
W / Be	3.551 (3.500)	1.679 (2.000)	2.333 (2.000)
N1	-2.473(-3)		-2.473
N2	-3.714 (-3)		-2.626
N3		-3.4285 (-3)	

Solid State MAS NMR spectroscopy



Figure S4.5. Solid state MAS NMR spectra of 9 Be of W₂Be₄N₅ at a spinning frequency of 12 kHz confirming the presence of Be inside the sample. Spinning side-bands are marked with asterisks.

FTIR spectroscopy



Figure S4.6. FTIR spectrum of W₂Be₄N₅. No N–H valence bonds are visible. The overall slope originates from the strong color of the sample.

Crystallographic information for $W_4Be_8N_9$

Formula	W ₄ Be ₈ N ₉
Crystal system	trigonal
Space group	<i>R</i> 3 <i>m</i> (no. 166)
Lattice parameters / Å	<i>a</i> = 2.8647(3)
	<i>c</i> = 67.273(7)
Cell volume /ų	478.11(11)
Formula units per unit cell	3
Density / g cm ⁻³	9.727
Molecular weight / g mol ⁻¹	933.57
Linear absorption coefficient / mm ⁻¹	71.913
T _{min} /T _{max}	0.6656
Diffractometer	D8 Venture
Radiation	Mo-Kα ₁ (λ = 0.71973 Å)
Absorption correction	multi-scan
F(000)	1173
θ range / °	$3.634 \le \theta \le 30.477$
Total no. of reflections	2548
Independent reflections $[I \ge 2\sigma(I)/all]$	235/254
R _{int}	0.043
Refined parameters	25
Goodness of fit	1.232
<i>R</i> -values $[l \ge 2\sigma(l)]$	$R_1 = 0.0259; wR2 = 0.0643$
<i>R</i> -values [all data]	$R_1 = 0.0283; wR2 = 0.0654$
$\Delta ho_{ m max}$, $\Delta ho_{ m min}$ / e Å 3	2.81; -4.47

Table S4.5. Crystallographic data of W₄Be₈N₉. Standard deviations are given in parenthesis.

Atom	Wyck.	x	у	Z	U _{eq} / Ų	Occ.
W1	6 <i>c</i>	0	0	0.46258(2)	0.0052(2)	1
W2	6 <i>c</i>	0	0	0.38770(2)	0.0070(1)	1
N1	6 <i>c</i>	0	0	0.10998(17)	0.005(2)	1
N2	6 <i>c</i>	0	0	0.14893(19)	0.008(3)	1
N3	6 <i>c</i>	0	0	0.25937(19)	0.008(2)	1
N4	6 <i>c</i>	0	0	0.29853(17)	0.002(2)	1
N5	3 <i>a</i>	0	0	0	0.003(3)	1
Be1	6 <i>c</i>	0	0	0.3230(6)	0.046(9)	1
Be2	6 <i>c</i>	0	0	0.0870(5)	0.033(7)	1
Be3	6 <i>c</i>	0	0	0.169(1)	0.084(18)	1
Be4	6 <i>c</i>	0	0	0.2369(11)	0.09(2)	1

Table S4.6. Wyckoff positions, coordinates, isotropic thermal displacement parameters and occupancy of $W_4Be_8N_9$. Standard deviations are given in parenthesis.

Table S4.7. Anisotropic displacement parameters for W in $W_4Be_8N_9$. Standard deviations are given in parenthesis.

Atom	U ₁₁ /Ų	U ₂₂ / Ų	U ₃₃ / Ų	U ₁₂ / Ų	U ₁₃ / Ų	U ₂₃ / Ų
W1	0.0034(3)	0.0034(3)	0.0087(3)	0.00170(13)	0	0
W2	0.0055(2)	0.0055(2)	0.0100(3)	0.00276(12)	0	0

Crystal structure of $W_4Be_8N_9$ and its comparison to $W_2Be_4N_5$



Figure S4.7. Crystal structure of W₄Be₈N₉ (left, c = 67.273(7) Å) compared to the structure of W₂Be₄N₅ (right, c = 37.0753(13) Å). For both structures, the stacking order ABC can be divided into different sublayers. The "a" sublayer of W₄Be₈N₉ consist of three "a" sublayers of W₂Be₄N₅ (marked with an "x" between the two structures).





Figure S4.8. Temperature dependent powder X-ray diffraction pattern (Ag-K α_1 radiation, $\lambda = 0.55942$ Å) of W₂Be₄N₅ measured under Ar atmosphere up to 900 °C. No significant change in the unit cell can be observed. At 800 °C a weak reflection at 12° appears, that may arise from a starting decomposition. However, the original compound stays stable up to 900 °C.



Figure S4.9. Temperature-dependent evolution of the cell volume and the lattice parameters of W₂Be₄N₅ with linear fits ($\alpha_a = 6.3(2)$; $\alpha_c = 9.6(7)$; $\alpha_v = 22.4(7)$ ppm K⁻¹).



Figure S4.10. Temperature dependent powder X-ray diffraction pattern (Ag-K α_1 radiation, $\lambda = 0.55942$ Å) of a sample that consist of W₂Be₄N₅ and W₄Be₈N₉ measured under Ar atmosphere up to 900 °C. Both compounds stay stable until 750 °C. At this temperature, the decomposition in WO₃ can be observed, what might arise from the reaction with the silica capillary. A pure sample of W₂Be₄N₅ stays stable up to at least 800 °C (see Figure S8). A phase transition from one compound into the other cannot be observed.
Magnetic measurements



Figure S4.11. Magnetic susceptibility vs temperature plots of a sample of $W_2Be_4N_5$ measured at an external field *H* of 0.1 T (a, left) and 3 T (b, right). The data collected shows a very weak paramagnetic signal with a small temperature dependence. This signal likely arises from ferromagnetic impurities.



Figure S4.12. Magnetization vs. applied field plots for a sample of W_2N_3 (a). The diamagnetic behavior becomes apparent, especially in the magnification for 300 K (b). The susceptibility vs. temperature measurements (c and d) show a paramagnetic behavior, which likely arises from paramagnetic impurities.

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8.4 Supporting Information for Chapter 5

Experimental Procedures

Safety notice

Beryllium and its compounds can cause diseases like acute berylliosis, chronic beryllium disease (CBD), contact dermatitis and cancer. Especially the inhalation of Be containing dust or contact with solvable Be salts is dangerous. Consequently, the complete handling of starting materials and Be containing samples was carried out in a designated glovebox. Samples outside the glovebox were only transported in closed vessels. For unavoidable work with Be outside the glovebox (e.g. cleaning working equipment) care must be taken to additional safety precautions like FFP3-masks and the avoidance of dusts. This is especially important for the synthesis of bulk materials used as starting material for the high-pressure experiments. The danger in the Diamond Anvil Cell experiment itself is far lower, since the single crystal we prepared in the experiment exhibits a mass of approx. 5 ng. Guidelines how to work with Be are available in the literature.^[1-2]

High-pressure high-temperature synthesis of W₂Be₄N₅

The sample of $W_2Be_4N_5$ used for the DAC experiment was synthesized as already described previously in a high-temperature high-pressure approach in a hydraulic 1000 t press utilizing the multianvil technique with a modified Walker module.^[3-5] First, a MgO octahedron was prepared as follows: A ZrO₂ cylinder, equipped with two graphite furnaces and MgO spacers was placed in the center of a cylindrical hole drilled into the MgO octahedron (5% Cr₂O₃ doped MgO, 18 mm edge length, Ceramic Substrates & Components Ltd, Isle of Wight). The graphite furnaces were contacted with Mo plates. Stoichiometric amounts of Be_3N_2 (17.0 mg, 0.310 mmol), W (85.4 mg, 0.464 mmol) and NaN₃ (15.1 mg, 0.232 mmol) were ground in a tungsten carbide mortar in a glovebox (see above). The mixture was packed in an h-BN crucible (Henze, Kempten) and transferred into the MgO octahedron. The filled octahedron was placed in the void formed by eight tungsten carbide cubes with truncated corners, which were separated with pyrophyllite gaskets. The assembly was transferred to the multianvil apparatus and compressed to 8 GPa within 240 min. At this pressure the sample was heated to 1350 °C within 35 min, kept at this temperature for 15 min and cooled down to room temperature within 15 min before the pressure was decreased to ambient pressure within 720 min. The recovered sample was washed with water to remove residual reactants and analyzed using powder X-ray diffraction. Suitable single crystals were selected and assessed by single-crystal X-ray diffraction.

Laser-heated diamond anvil cell (LH-DAC)

High-pressure experiments were carried out in a Boehler-Almax BX90 diamond anvil cell (DAC) with an opening angle of 60°, equipped with a pair of Boehler-Almax diamonds with a culet size of 250 μ m.^[6] The anvils were separated by a Re gasket with a laser-drilled hole of 100 μ m, forming the sample chamber. The cell was loaded with a single crystal of W₂Be₄N₅ and a piece of ruby. Ne served as a pressure transmitting medium and pressure gauge. The cell was compressed to 41.0(1) GPa in seven steps at ambient temperature. At each pressure point, sc-XRD data was

collected (see below). At the target pressure, the sample was heated from both sides using a nearinfrared (NIR) fiber laser ($\lambda = 1064$ nm, focused to 20x20 μ m²). After a bright flash occurred, the sample was cooled down to ambient temperature and XRD data were collected. The temperature was likely above 3000 K based on previous observations but was not precisely determined.

Single crystal X-ray diffraction with Synchrotron radiation

Pressure dependent single-crystal X-ray diffraction (sc-XRD) data of $W_2Be_4N_5$ and $BeW_{10}N_{14}(N_2)$ were collected at the Extreme Conditions Beamline P02.2 (PETRA III) at DESY in Hamburg ($\lambda = 0.2905$ Å, Perkin Elmer XRD1621 flat panel detector).^[7-8] The beam diameter was 1.8x1.4 μ m². The laser heated sample area was surveyed by acquiring still-images on a regularly spaced grid. Afterwards, on selected points of the grid, sc-XRD data were collected while rotating the DAC around the vertical axis of the goniometer ω in a range from -32° to $+32^{\circ}$ with a scanning step of 0.5°. For the pressure determination, powder XRD data was obtained by radial integration of single frames using Dioptas.^[9] After identification of the reflections of Ne and a subsequent Pawley fit, the pressure was determined using the equation of state of Ne.^[10-11]

Data analysis of the multi domain measurements was conducted using the CrysAlisPro software and the Domain Auto Finder.^[12-13] Structure solution and subsequent refinement was carried out with SHELXL, respectively.^[14-15] Structures were visualized using VESTA.^[16]

Equation of State

Using the pressure-volume data from pressure-dependent single crystal refinements of $W_2Be_4N_5$ from ambient pressure to 41.0(1) GPa, the decrease of the unit cell volume was fitted by a 2nd order Birch-Murnaghan equation of state with the program package EoSFit7.^[17-19] The results of the DFT calculations for the elastic properties of BeW₁₀N₁₄(N₂) were fitted using a 3rd order Birch-Murnaghan equation of state (Equation 5.1). The results were plotted using Origin.^[20]

$$p(V) = \frac{3}{2} K_0 \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \cdot \left[1 + \frac{3}{4} (K_0' - 4) \left\{ \left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right\} \right]$$
(5.1)

 $(K_0: isothermal bulk modulus, V_0: unit cell volume at a theoretical pressure of 0 GPa, V: unit cell volume, K_0' partial pressure derivative of the isothermal bulk modulus)$

DFT calculations

First-principles calculations were carried out within the framework of density functional theory (DFT), employing the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional and the plane wave/pseudopotential approach implemented in the CASTEP simulation package.^[21-23] "On the fly" norm-conserving pseudopotentials generated using the descriptors in the CASTEP database, were employed in conjunction with plane waves up to a kinetic energy cutoff of 990 eV. The accuracy of the pseudopotentials is well established.^[24] A Monkhorst–Pack grid was used for Brillouin zone integrations.^[25] We used a distance between grid points of <0.023 Å⁻¹. Convergence criteria for geometry optimization included an energy change of <5 × 10–6 eV atom⁻¹ between

steps, a maximal force of <0.01 eV Å⁻¹ and a maximal component of the stress tensor <0.02 GPa. The elastic stiffness tensor was computed by stress-strain calculations.

Results and Discussion



Redetermination of the crystal structure of W₂Be₄N₅

Figure 5.1. Refined crystal structure of $W_2Be_4N_5$ along [001] and the coordination polyhedra W1, Be1 and Be2 (left). The structure consists of layers of WN₆ trigonal prisms that are separated by layers of edge-sharing BeN₄ tetrahedra. W: gray; Be: green, N: blue.

The redetermination of the crystal structure of $W_2Be_4N_5$ at ambient pressure confirmed the structural model, which we had found before. A detailed description of the crystal structure was already reported elsewhere.^[3] However, it is worth mentioning, that the bonding distance Be1–N3 of 1.62(4) Å is longer than reported before (1.53(3) Å) and identical to the bond distance Be2–N1 of 1.68(3) Å within the experimental errors. These findings are consistent with the more precise CHARDI calculations of $W_2Be_4N_5$, which can be found in Table S4.

Formula	W ₂ Be ₄ N ₅
Crystal system	trigonal
Space group	<i>R</i> 3 <i>m</i> (no. 166)
Lattice parameters / Å	<i>a</i> = 2.8702(2)
	<i>c</i> = 37.1324(18)
Cell volume / ų	264.92(2)
Formula units per unit cell	3
Density / g cm ⁻³	8.909
Molecular weight / g mol ⁻¹	473.79
Linear absorption coefficient / mm ⁻¹	6.197
Diffractometer	P02.2 (DESY)
Wavelength / Å	0.2905
Absorption correction	multi-scan
F(000)	597
heta range / °	$4.032 \le \theta \le 17.537$
Total no. of reflections	318
Independent reflections $[l \ge 2\sigma(l)/all]$	175/181
R _{int}	0.017
Refined parameters	17
Goodness of fit	1.085
<i>R</i> -values $[I \ge 2\sigma(I)]$	$R_1 = 0.0254; wR2 = 0.0617$
R-values [all data]	$R_1 = 0.0269; wR2 = 0.0625$
Δho_{max} , Δho_{min} / e Å ³	4.28; –2.92

Table S5.1. Crystallographic data of W₂Be₄N₅. Standard deviations are given in parentheses.

Table S5.2. Wyckoff positions, coordinates, isotropic thermal displacement parameters and occupancies in $W_2Be_4N_5$. Standard deviations are given in parentheses.

Atom	Wyck.	x	у	Ζ	U _{eq} / Ų	Occ.
W1	6 <i>c</i>	0	0	0.06791(2)	0.0056(1)	1
N1	6 <i>c</i>	0	0	0.2308(2)	0.0072(10)	1
N2	3 <i>c</i>	0	0	1/2	0.0074(14)	1
N3	6 <i>c</i>	0	0	0.30107(17)	0.0048(9)	1
Be1	6 <i>c</i>	0	0	0.3447(9)	0.046(7)	1
Be2	6 <i>c</i>	0	0	0.1856(6)	0.028(4)	1

Atom	U ₁₁ /Ų	U ₂₂ / Ų	U ₃₃ / Ų	U ₁₂ / Ų	U ₁₃ / Ų	U ₂₃ / Ų
W1	0.00245(16)	0.00245(16)	0.01176(19)	0.00123(8)	0	0
N1	0.0048(17)	0.0048(17)	0.012(2)	0.0024(9)	0	0
N2	0.006(2)	0.006(2)	0.010(3)	0.0029(12)	0	0
N3	0.0041(15)	0.0041(15)	0.0062(19)	0.0021(8)	0	0

 $\label{eq:stable} \textbf{Table S5.3.} An isotropic displacement parameters for W and N in W_2Be_4N_5. Standard deviations are given in parentheses.$

Charge distribution (CHARDI)

Table S5.4: Results of the CHARDI analysis for $W_2Be_4N_5$.

Polyhedron	W N1 N1 N1 N3 N3 N3	Be1 N3 N3 N3 N3	Be2 N1 N2 N2 N2
Average bong length / Å	2.1091	1.774	1.7697
Polyhedral volume / Å ³	9.3078	2.8490	2.8317
Distortion index (bond length)	0.00557	0.04424	0.02579
Quadratic elongation	-	1.0102	1.0038
Bond angle variance / ° ²	-	41.7124	15.8005
Effective coordination number	5.9936	3.3456	3.8277
Total charge (theory)			
W / Be	3.570 (3.500)	1.741 (2.000)	2.305 (2.000)
N1	-2.472(-3)		-2.472
N2	-3.691 (-3)		-2.674
N3		-3.4095 (-3)	



Elastic properties of W₂Be₄N₅

Figure S5.2. Pressure-volume data with a fit using a 2^{nd} order Birch-Murnaghan equation of state (left) and the evolution of the lattice parameters of W₂Be₄N₅ with increasing pressure (right). Error bars are smaller than the symbol size.

The bulk modulus of $W_2Be_4N_5$ was determined using the pressure-volume data based on sc-XRD refinements at different pressure points. The data was fitted with a 2nd order Birch-Murnaghan equation of state (Figure S2) with the fitting parameters $V_0 = 264.28(2)$ Å³, $K_0 = 273.4(11)$ GPa and a fixed value for K' of 4.0. Additionally, the relative evolution of the lattice parameters with increasing pressure was examined (Figure S2). The pressure-induced shortening of the lattice parameters is similar for the *a*- and *c*-axis until about 25 GPa, when the *c*-axis becomes slightly more compressible. No pressure-induced phase transition was observed and $W_2Be_4N_5$ stays stable up to 41.0(1) GPa on cold compression. At this point, the sample was heated.

Crystallographic information for $BeW_{10}N_{14}(N_2)$

Formula		BeW ₁₀ N ₁₄ (N ₂)	
Crystal system		monoclinic	
Space group		<i>C</i> 2/ <i>m</i> (no. 12)	
Lattice parameters / Å, °	<i>a</i> = 20.69(3)	<i>a</i> = 20.554(2)	<i>a</i> = 19.803(5)
	<i>b</i> = 2.8666(4)	b = 2.8457(4)	b = 2.7867(6)
	<i>c</i> = 8.539(12)	<i>c</i> = 8.324(7)	<i>c</i> = 8.2467(15)
	$\beta = 100.69(15)$	β = 99.59(3)	$\beta = 99.605(19)$
Cell volume /ų	497.7(1)	480.1(4)	448.72(17)
Pressure / GPa	0	16.5(1)	42.1(1)
Formula units per unit cell		2	
Density / g cm ⁻³	13.824	14.331	15.332
Molecular weight / g mol ⁻¹		2071.67	
Linear absorption coefficient / mm ⁻¹	10.958	11.359	12.154
Beamline		P02.2 (DESY)	
Wavelength / Å		0.2905	
F(000)		1712	
heta range / °	$2.327 \leq \theta \leq 17.291$	$1.643 \leq \theta \leq 17.797$	$2.436 \le \theta \le 17.728$
Total no. of reflections	758	1006	926
Independent reflections $[I \ge 2\sigma(I)/all]$	256/510	397/577	478/591
R _{int}	0.090	0.043	0.057
Refined parameters	49	56	56
Goodness of fit	1.053	0.968	1.137
<i>R</i> -values $[l \ge 2\sigma(l)]$	$R_1 = 0.087; wR2 = 0.157$	$R_1 = 0.046; wR2 = 0.097$	$R_1 = 0.064; wR2 = 0.148$
R-values [all data]	$R_1 = 0.189; wR2 = 0.197$	$R_1 = 0.083; wR2 = 0.109$	$R_1 = 0.082; wR2 = 0.164$
$\Delta ho_{ m max}$, $\Delta ho_{ m min}$ / e Å ³	5.07; –5.21	3.93; –3.42	6.15; –4.71

Table S5.5. Crystallographic data of $BeW_{10}N_{14}(N_2)$ at different pressure points. Standard deviations are given in parentheses.

Atom	Wyck.	x	у	Z	U _{eq} / Ų	Occ.
W1	4 <i>i</i>	0.17043(5)	0	0.4744(3)	0.0057(7)	1
W2	4 <i>i</i>	0.55455(5)	0	0.3115(3)	0.0064(7)	1
W3	4 <i>i</i>	0.62640(5)	0	0.0433(3)	0.0064(7)	1
W4	4 <i>i</i>	0.09242(5)	0	0.7337(3)	0.0073(7)	1
W5	4 <i>i</i>	0.76901(5)	0	0.1974(3)	0.0130(10)	1
N1	4 <i>i</i>	0.2622(9)	0	0.381(6)	0.006(3)	1
N2	4 <i>i</i>	0.6544(10)	0	0.310(7)	0.012(4)	1
N3	4 <i>i</i>	0.0620(11)	0	0.121(8)	0.012(4)	1
N4	4 <i>i</i>	0.0000(12)	0	0.418(7)	0.013(4)	1
N5	4 <i>i</i>	0.3951(10)	0	0.458(6)	0.007(3)	1
N6	4 <i>i</i>	0.3402(9)	0	0.160(6)	0.008(3)	1
N7	4 <i>i</i>	0.2052(11)	0	0.080(7)	0.013(4)	1
N8	4 <i>i</i>	0.4563(11)	0	0.167(7)	0.012(4)	1
Be1	2 <i>b</i>	0	1/2	0	0.05(3)	1

Table S5.6. Wyckoff positions, coordinates, isotropic thermal displacement parameters and occupancies in $BeW_{10}N_{14}(N_2)$ at 16.5(1) GPa. Standard deviations are given in parentheses.

Table S5.7. Anisotropic displacement parameters for W in $BeW_{10}N_{14}(N_2)$ at 16.5(1) GPa. Standard deviations are given in parentheses.

Atom	U ₁₁ /Å ²	U ₂₂ / Ų	U ₃₃ / Ų	U ₁₂ / Ų	U ₁₃ / Ų	U ₂₃ / Ų
W1	0.0103(4)	0.0046(4)	0.002(2)	0	0.0007(6)	0
W2	0.0104(4)	0.0043(4)	0.004(2)	0	-0.0006(6)	0
W3	0.0104(4)	0.0045(4)	0.004(2)	0	0.0006(6)	0
W4	0.0107(4)	0.0053(4)	0.005(2)	0	-0.0009(6)	0
W5	0.0144(4)	0.0084(4)	0.014(3)	0	-0.0036(7)	0

Atom	Wyck.	x	у	Z	U _{eq} / Ų	Occ.
W1	4 <i>i</i>	0.17015(9)	0	0.4671(2)	0.0078(5)	1
W2	4 <i>i</i>	0.55232(9)	0	0.3015(2)	0.0079(5)	1
W3	4 <i>i</i>	0.62261(9)	0	0.0292(2)	0.0074(5)	1
W4	4 <i>i</i>	0.09578(9)	0	0.7250(2)	0.0077(5)	1
W5	4 <i>i</i>	0.76122(11)	0	0.2089(3)	0.0147(7)	1
N1	4 <i>i</i>	0.266(2)	0	0.386(4)	0.008(5)	1
N2	4 <i>i</i>	0.6582(19)	0	0.293(4)	0.007(5)	1
N3	4 <i>i</i>	0.0590(18)	0	0.113(4)	0.006(4)	1
N4	4 <i>i</i>	-0.002(3)	0	0.416(6)	0.017(7)	1
N5	4 <i>i</i>	0.398(2)	0	0.463(6)	0.015(7)	1
N6	4 <i>i</i>	0.336(2)	0	0.178(5)	0.012(6)	1
N7	4 <i>i</i>	0.201(2)	0	0.059(5)	0.012(6)	1
N8	4 <i>i</i>	0.456(2)	0	0.160(5)	0.011(5)	1
Be1	2 <i>b</i>	0	1/2	0	0.09(9)	1

Table S5.8. Wyckoff positions, coordinates, isotropic thermal displacement parameters and occupancies in $BeW_{10}N_{14}(N_2)$ at 42.1(1) GPa Standard deviations are given in parentheses.

Table S5.9. Anisotropic displacement parameters for W in $BeW_{10}N_{14}(N_2)$ at 42.1(1) GPa. Standard deviations are given in parentheses.

Atom	U ₁₁ /Ų	U ₂₂ / Å ²	U ₃₃ / Ų	U ₁₂ / Å ²	U ₁₃ / Ų	U ₂₃ / Ų
W1	0.0087(11)	0.0056(9)	0.0091(8)	0	0.0016(7)	0
W2	0.0109(11)	0.0047(9)	0.0080(8)	0	0.0014(7)	0
W3	0.0089(11)	0.0056(9)	0.0076(8)	0	0.0013(7)	0
W4	0.0107(11)	0.0047(9)	0.0075(8)	0	0.0011(7)	0
W5	0.0160(14)	0.0105(11)	0.0166(11)	0	-0.0004(9)	0

Atom	Wyck.	X	у	Z	U _{eq} / Ų	Occ.
W1	4 <i>i</i>	0.1701(3)	0	0.4712(8)	0.010(2)	1
W2	4 <i>i</i>	0.5531(3)	0	0.3080(8)	0.012(3)	1
W3	4 <i>i</i>	0.6232(3)	0	0.0356(8)	0.012(2)	1
W4	4 <i>i</i>	0.0950(3)	0	0.7268(8)	0.011(2)	1
W5	4 <i>i</i>	0.7653(6)	0	0.2015(12)	0.034(4)	1
N1	4 <i>i</i>	0.264(7)	0	0.385(15)	0.006(3)	1
N2	4 <i>i</i>	0.646(6)	0	0.298(15)	0.006(3)	1
N3	4 <i>i</i>	0.060(6)	0	0.118(14)	0.006(3)	1
N4	4 <i>i</i>	-0.006(6)	0	0.402(14)	0.006(3)	1
N5	4 <i>i</i>	0.379(6)	0	0.411(15)	0.006(3)	1
N6	4 <i>i</i>	0.334(7)	0	0.158(16)	0.006(3)	1
N7	4 <i>i</i>	0.184(6)	0	0.034(15)	0.006(3)	1
N8	4 <i>i</i>	0.457(7)	0	0.178(15)	0.006(3)	1
Be1	2 <i>b</i>	0	1/2	0	0.11(16)	1

Table S5.10. Wyckoff positions, coordinates, isotropic thermal displacement parameters and occupancies in $BeW_{10}N_{14}(N_2)$ at 0 GPa. Standard deviations are given in parentheses.

Table S5.11. Anisotropic displacement parameters for W in $BeW_{10}N_{14}(N_2)$ at 0 GPa. Standard deviations are given in parentheses.

Atom	U ₁₁ /Å ²	U ₂₂ / Ų	U ₃₃ / Ų	U ₁₂ / Ų	U ₁₃ / Ų	U ₂₃ / Å ²
W1	0.005(4)	0.0005(7)	0.026(5)	0	0.007(5)	0
W2	0.016(5)	0.0025(8)	0.018(6)	0	0.008(5)	0
W3	0.014(5)	0.0036(8)	0.021(5)	0	0.008(5)	0
W4	0.013(5)	0.0029(8)	0.017(5)	0	0.004(5)	0
W5	0.029(9)	0.0055(10)	0.059(8)	0	-0.012(7)	0



Figure S5.3. (*hk*0)-reciprocal lattice plane of BeW₁₀N₁₄(N₂) at 16.5(1) GPa with indexed reflections. All reflections fulfill the reflection condition h + k = 2n for the *C*-centering. Additional reflections arise from unreacted starting material W₂Be₄N₅, the pressure transmitting medium Ne and the side phase W₂N₃.^[3, 26]



Figure S5.4. (*h*-2*l*)-reciprocal lattice plane of BeW₁₀N₁₄(N₂) at 16.5(1) GPa with indexed reflections. All reflections fulfill the reflection condition h + k = 2n for the *C*-centering. Additional reflections arise from unreacted starting material W₂Be₄N₅, the pressure transmitting medium Ne and the side phase W₂N₃.^[3, 26]



Figure S5.5. Azimuthal integrated data, powder diffraction pattern and Le Bail fit of BeW₁₀N₁₄(N₂) at 16.5(1) GPa. Positions of Bragg reflections of BeW₁₀N₁₄(N₂) and Ne are given as blue and green bars, respectively ($\lambda = 0.2905$ Å).

DFT calculations

	/537.29	208.7	240	0	21.545	0 \
1	208.7	585.34	289.76	0	-49.144	0
	240	289.76	433.44	0	25.453	0
	0	0	0	184.36	0	-41.033
	21.545	-49.144	25.453	0	180.86	0 /
	\ 0	0	0	-41.033	0	174.95 /

Figure S5.3. Elastic stiffness matrix for BeW₁₀N₁₄(N₂). Values are given in GPa. Its evaluation with the program ELATE reveals an isothermal bulk modulus $K_0 = 337$ GPa, implying that this compound is ultra-incompressible.^[27]



Figure S5.4. Density of States of $BeW_{10}N_{14}(N_2)$. The calculation shows no band gap and thus, the system is metallic.

Table S5.12. Calculated Mulliken charges in $BeW_{10}N_{14}(N_2)$. The calculated value of N4 differs from the values of the other nitrogen atoms due to the formation of the $[N_2]$ dumbbell.

Atoms	Mulliken charge
W1	0.914
W2	0.920
W3	0.901
W4	0.937
W5	0.943
N1	-0.610
N2	-0.597
N3	-0.684
N4*	-0.447
N5	-0.613
N6	-0.606
N7	-0.667
N8	-0.665
Be1	0.545

Formula	BeW ₁₀ N ₁₄ (N ₂)				
Crystal system	monoclinic				
Space group	<i>C</i> 2/ <i>m</i> (no. 12)				
Lattice parameters / Å, °	<i>a</i> = 21.2258	<i>a</i> = 20.4120			
	<i>b</i> = 2.8415	<i>b</i> = 2.7636			
	<i>c</i> = 8.5983	<i>c</i> = 8.2749			
	β = 100.9854	$\beta = 100.7552$			
Cell volume /ų	509.09	458.59			
Pressure / GPa	0	45			
Formula units per unit cell		2			
Density / g cm ⁻³	13.514	15.002			
Molecular weight / g mol ⁻¹	207	71.67			

Table S5.13. Crystallographic data of $BeW_{10}N_{14}(N_2)$ at 0 and 45 GPa derived from DFT calculations.

Table S5.14. Wyckoff positions, coordinates, isotropic thermal displacement parameters and occupancies in $BeW_{10}N_{14}(N_2)$ at 0 GPa derived from DFT calculations.

Atom	Wyck.	X	у	Z	U _{eq} / Ų	Occ.
W1	4 <i>i</i>	0.16876	0	0.47309	0.0060	1
W2	4 <i>i</i>	0.55300	0	0.31178	0.0072	1
W3	4 <i>i</i>	0.62616	0	0.04524	0.0067	1
W4	4 <i>i</i>	0.09305	0	0.73310	0.0077	1
W5	4 <i>i</i>	0.76901	0	0.20407	0.0138	1
N1	4 <i>i</i>	0.26046	0	0.38369	0.007	1
N2	4 <i>i</i>	0.64902	0	0.29819	0.013	1
N3	4 <i>i</i>	0.05896	0	0.11910	0.012	1
N4	4 <i>i</i>	0.00045	0	0.58416	0.013	1
N5	4 <i>i</i>	0.39522	0	0.45979	0.008	1
N6	4 <i>i</i>	0.33833	0	0.16383	0.007	1
N7	4 <i>i</i>	0.20431	0	0.07935	0.013	1
N8	4 <i>i</i>	0.45459	0	0.15486	0.011	1
Be1	2 <i>b</i>	0	1/2	0	0.100	1

Atom	U ₁₁ /Ų	U ₂₂ / Ų	U ₃₃ / Ų	U ₁₂ / Ų	U ₁₃ / Ų	U ₂₃ / Ų
W1	0.01099	0.00449	0.00212	0.00000	0.00053	0.00000
W2	0.01099	0.00439	0.00529	0.00000	-0.00053	0.00000
W3	0.01099	0.00449	0.00423	0.00000	0.00063	0.00000
W4	0.01142	0.00528	0.00529	0.00000	-0.00116	0.00000
W5	0.01543	0.00838	0.01481	0.00000	-0.00402	0.00000

Table S5.15. Anisotropic displacement parameters for W in $BeW_{10}N_{14}(N_2)$ at 0 GPa derived from DFT calculations.

Table S5.16. Wyckoff positions, coordinates, isotropic thermal displacement parameters and occupancies in $BeW_{10}N_{14}(N_2)$ at 45 GPa derived from DFT calculations.

Atom	Wyck.	x	у	Z	U _{eq} / Ų	Occ.
W1	4 <i>i</i>	0.16967	0	0.47258	0.0055	1
W2	4 <i>i</i>	0.55283	0	0.30810	0.0067	1
W3	4 <i>i</i>	0.62520	0	0.04096	0.0062	1
W4	4 <i>i</i>	0.09292	0	0.73037	0.0071	1
W5	4 <i>i</i>	0.76811	0	0.19980	0.0128	1
N1	4 <i>i</i>	0.26030	0	0.38380	0.007	1
N2	4 <i>i</i>	0.65183	0	0.29241	0.013	1
N3	4 <i>i</i>	0.05773	0	0.11495	0.012	1
N4	4 <i>i</i>	0.00015	0	0.58396	0.013	1
N5	4 <i>i</i>	0.39614	0	0.46012	0.008	1
N6	4 <i>i</i>	0.33786	0	0.16763	0.007	1
N7	4 <i>i</i>	0.20467	0	0.06757	0.013	1
N8	4 <i>i</i>	0.45621	0	0.15616	0.010	1
Be1	2 <i>b</i>	0	1/2	0	0.010	1

Table S5.17. Anisotropic displacement parameters for W in $BeW_{10}N_{14}(N_2)$ at 45 GPa derived from DFT calculations.

Atom	U ₁₁ /Ų	U ₂₂ / Ų	U ₃₃ / Ų	U ₁₂ / Å ²	U ₁₃ / Ų	U ₂₃ / Ų
W1	0.01018	0.00424	0.00196	0.00000	0.00049	0.00000
W2	0.01018	0.00415	0.00491	0.00000	-0.00049	0.00000
W3	0.01018	0.00424	0.00392	0.00000	0.00059	0.00000
W4	0.01057	0.00500	0.00491	0.00000	-0.00108	0.00000
W5	0.01429	0.00792	0.01373	0.00000	-0.00372	0.00000

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9 Miscellaneous

9.1 List of publications within this Thesis

1. Highly Condensed and Super-Incompressible Be₂PN₃

Georg Krach, Jennifer Steinadler, Kristian Witthaut, Wolfgang Schnick

Published in: *Angew. Chem. Int. Ed.* **2024**, *63*, e202404953 Access via: DOI: <u>10.1002/anie.202404953</u>

The synthesis, structural analysis and data evaluation were performed by Georg Krach. NMR experiments were conducted by Jennifer Steinadler. DFT calculations were performed by Kristian Witthaut. Georg Krach wrote the manuscript and Wolfgang Schnick supervised the project. All authors contributed to the discussion of the results and revised the manuscript.

2. Synthesis and Comprehensive Studies of Be-IV-N₂ (IV = Si, Ge): Solving the Mystery of Wurtzite-type *Pmc*2₁ Structures

<u>Georg Krach</u>, Kristian Witthaut, Jennifer Steinadler, Thomas Bräuniger, Victor Milman, Lkhamsuren Bayarjargal, Björn Winkler, Elena Bykova, Maxim Bykov, Wolfgang Schnick

> Published in: *Angew. Chem. Int. Ed.* **2024**, *63*, e202409593 Access via: DOI: <u>10.1002/anie.202409593</u>

The syntheses, structural analysis and data evaluation were performed by Georg Krach. NMR experiments were conducted by Jennifer Steinadler and supervised by Thomas Bräuniger. DFT calculations were performed by Kristian Witthaut, Victor Milman and Björn Winkler. Lkhamsuren Bayarjargal performed Raman measurements. Georg Krach, Elena Bykova and Maxim Bykov probed the high-pressure behavior of BeSiN₂. Georg Krach wrote the manuscript and Wolfgang Schnick supervised the project. All authors contributed to the discussion of the results and revised the manuscript.

3. Combination of Ambient and High-Temperature Beryllium Nitride Motifs in $W_2Be_4N_5$ and $W_4Be_8N_9$

Georg Krach, Dominik Werhahn, Kristian Witthaut, Dirk Johrendt, Wolfgang Schnick

Published in: *Angew. Chem. Int. Ed.* **2025**, *64*, e202420583 Access via: DOI: <u>10.1002/anie.202420583</u>

The syntheses, structural analysis and data evaluation were performed by Georg Krach. Dominik Werhahn and Kristian Witthaut performed VSM measurement. Georg Krach wrote the manuscript and Dirk Johrendt and Wolfgang Schnick supervised the project. All authors contributed to the discussion of the results and revised the manuscript. 4. High-Pressure Synthesis of Ultra-Incompressible Beryllium Tungsten Nitride Pernitride $BeW_{10}N_{14}(N_2)$

<u>Georg Krach</u>, Lukas Brüning, Sebastian Ambach, Elena Bykova, Nico Giordano, Björn Winkler, Maxim Bykov, Wolfgang Schnick

> Published in: *Angew. Chem. Int. Ed.* **2025**, e202505778 Access via: DOI: <u>10.1002/anie.202505778</u>

The synthesis and structural analysis were performed by Georg Krach, Lukas Brüning, Sebastian Ambach, Elena Bykova, Nico Giordano and Maxim Bykov. Data evaluation was performed by Georg Krach. DFT calculations were performed by Björn Winkler. Georg Krach wrote the manuscript and Maxim Bykov and Wolfgang Schnick supervised the project. All authors contributed to the discussion of the results and revised the manuscript.

9.2 List of Publications beyond this Thesis

- Synthesis and Crystal Structure of Silicon Pernitride SiN₂ at 140 GPa P.L. Jurzick, <u>G. Krach</u>, L. Brüning, W. Schnick, M. Bykov Acta. Crystallogr. 2023, E79, 923
- Building Nitridic Networks with Phosphorus and Germanium from Ge^{III}P₂N₄ to Ge^{IV}PN₃ S.J. Ambach, <u>G. Krach</u>, E. Bykova, K. Witthaut, N. Giordano, M. Bykov, W. Schnick *Inorg. Chem.* **2024**, *63*, 8502
- 3. High-pressure Synthesis of Ultra-incompressible, Hard and Superconducting Tungsten Nitrides

A. Liang, I. Osmond, <u>G. Krach</u>, L.-T. Shi, L. Brüning, U. Ranieri, J. Spender, F. Tasnadi, B.
Massani, C.R. Stevens, R.S. McWilliams, E. Lawrence Bright, N. Giordano, S. Gallego-Parra, Y.
Yin, A. Aslandukov, F.I. Akbar, E. Gregoryanz, A. Huxley, M. Peña-Alvarez, J.-G. Si, W. Schnick,
M. Bykov, F. Trybel, D. Laniel
Adv. Funct. Mater. 2024, 34, 2313819

 Investigation of the Binary Nitrides YN, LaN and LuN by Solid-State NMR Spectroscopy J. Steinadler, <u>G. Krach</u>, W. Schnick T. Bräuniger *Molecules* 2024, 29, 5572

9.3 Fundings

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9.4 Conference Contributions

Beryllium in Fusion Reactors

<u>Georg Krach</u>, Wolfgang Schnick Talk, Seminar Schnick Group, **2024**, Munich, Germany

Be under pressure

<u>Georg Krach</u>, Wolfgang Schnick Talk, 7. Obergurgl-Seminar Festkörperchemie, **2024**, Obergurgl, Austria

Wurtzite-Type Be₂PN₃ – a new and hard-type material

<u>Georg Krach</u>, Kristian Witthaut, and Wolfgang Schnick Poster, 11th International Symposium on Nitrides, **2023**, Prague, Czech Repuplic

Synthesis and Characterization of Be-IV-N₂ (IV = Si, Ge)

<u>Georg Krach</u>, Kristian Witthaut, and Wolfgang Schnick Poster, 18th European Conference on Solid State Chemistry, **2023**, Saint-Malo, France

Neue, ternäre Beryllium Nitride

<u>Georg Krach</u>, Wolfgang Schnick Talk, Seminar Schnick Group, **2023**, Munich, Germany

PN-networks – now available with Be

<u>Georg Krach</u>, Wolfgang Schnick Talk, 6. Obergurgl-Seminar Festkörperchemie, **2023**, Obergurgl, Austria

Nitrid-Analoga zu Beryllium-haltigen Mineralien

<u>Georg Krach</u>, Wolfgang Schnick Talk, Seminar Schnick Group, **2022**, Munich, Germany

Intermetallische Vorläufer für Nitridsynthesen

Georg Krach, Wolfgang Schnick

Talk, Seminar Schnick Group, 2021, Munich, Germany

9.5 Deposited Crystal Structures

The Crystallographic Information Files (CIF) of the investigated compounds are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures servide (http://www.ccdc.cam.ac.uk/structures) by quoting the corresponding deposition number.

Compound	CSD	
Be ₂ PN ₃	2337802	
BeGeN ₂	2353301	
$W_2Be_4N_5$	2390751	
$W_4Be_8N_9$	2390752	
W₂Be₄N₅ (synchrotron)	2418207	
BeW ₁₀ N ₁₄ (N ₂) (16.5 GPa)	2418208	