

## Nitrides

# Synthesis and Comprehensive Studies of Be-IV-N<sub>2</sub> (IV=Si, Ge): Solving the Mystery of Wurtzite-Type *Pmc2*<sub>1</sub> 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  $\beta$ -NaFeO<sub>2</sub> structure, although a second arrangement in space group *Pmc2*<sub>1</sub> is predicted to be a viable alternative. Despite extensive theoretical and experimental studies, this structure has so far remained undiscovered. Herein, we report on BeGeN<sub>2</sub> in a *Pmc2*<sub>1</sub> structure, synthesized from Be<sub>3</sub>N<sub>2</sub> and Ge<sub>3</sub>N<sub>4</sub> 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 BeSiN<sub>2</sub> 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 *Pmc2*<sub>1</sub> open the door to a new field of research on wurtzite-type related structures.

GaN and its doping varieties (Al<sub>x</sub>Ga<sub>y</sub>In<sub>1-x-y</sub>N) show favorable properties for optoelectronic applications and can be found, for example, in LEDs, power electronics or solar cells.<sup>[1-2]</sup> 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.<sup>[3]</sup> 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,<sup>[4-5]</sup> such nitride compounds can have the following stoichiometry: I-IV<sub>2</sub>-N<sub>3</sub>, II<sub>2</sub>-V-N<sub>3</sub> (Na<sub>2</sub>SiO<sub>3</sub>-type),<sup>[6-9]</sup> II-IV-N<sub>2</sub> ( $\beta$ -NaFeO<sub>2</sub>-type)<sup>[6,10-15]</sup> or II-VI-N<sub>4</sub> (enargite-type)<sup>[16]</sup> 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).<sup>[17-18]</sup> 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.<sup>[19]</sup> 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<sub>x</sub>Ga<sub>y</sub>In<sub>1-x-y</sub>N) like in (Mg,Zn)SnN<sub>2</sub>.<sup>[20-21]</sup> To the best of our knowledge, each of the wurtzite-type II-IV-N<sub>2</sub> Grimm-Sommerfeld analogous compounds crystallizes in the  $\beta$ -NaFeO<sub>2</sub> structure (space group *Pna2*<sub>1</sub>) or a wurtzite structure with disordered cation positions, although three different other arrangements, represented by the space groups *Pca2*<sub>1</sub>, *Pmn2*<sub>1</sub>, and *Pmc2*<sub>1</sub> are theoretically possible.<sup>[22-24]</sup> However, the arrangements in space groups *Pca2*<sub>1</sub> and *Pmn2*<sub>1</sub> break the octet rule of local charge neutrality and are therefore not favorable.<sup>[23-24]</sup> In contrast, the octet rule obeying *Pmc2*<sub>1</sub> structure was predicted as a promising second candidate for II-IV-N<sub>2</sub> analogous compounds.<sup>[25]</sup> Most recently, this modification was theoretically investigated for ZnSnN<sub>2</sub> with a calculated energy

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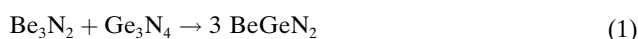
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difference between the known  $\beta$ -NaFeO<sub>2</sub> and the *Pmc*2<sub>1</sub> structure of only 13 meV.<sup>[26]</sup> Following, it was postulated that this small energy difference might be overcome during synthesis forming nanocrystalline regions of the *Pmc*2<sub>1</sub> structure, and Infrared and Raman spectra were theoretically calculated to analyze them.<sup>[27]</sup> However, the synthesis of a wurtzite-type nitride crystallizing solely in space group *Pmc*2<sub>1</sub> was not successful, so far.<sup>[19,26]</sup> One condition for compounds to favor the *Pmc*2<sub>1</sub> structure, stated in the literature, is that the ions occupying the II and IV position should have a very similar ionic radius.<sup>[19]</sup> A possible candidate for this requirement is BeSiN<sub>2</sub> (Be<sup>2+</sup>: 0.26 Å; Si<sup>4+</sup>: 0.27 Å).<sup>[28]</sup> However, this compound crystallizes in the  $\beta$ -NaFeO<sub>2</sub> structure as well.<sup>[10]</sup> Although the structure of BeSiN<sub>2</sub> is known since the 1960s, it was only part of several DFT studies but its optical properties have not been experimentally investigated, so far.<sup>[29–33]</sup> While heavier homologues, like MgGeN<sub>2</sub>, have already been synthesized, BeGeN<sub>2</sub> has only been studied theoretically.<sup>[30,32–34]</sup>

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 Be<sub>3</sub>N<sub>2</sub>. The synthesis of BeSiN<sub>2</sub>, starting from the binary nitrides, is carried out at temperatures higher than 1800 °C.<sup>[10]</sup> At this temperature, Ge<sub>3</sub>N<sub>4</sub> 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 Be<sub>3</sub>N<sub>2</sub> and its reaction with thermally labile, but high-pressure stabilized P<sub>3</sub>N<sub>5</sub> to synthesize highly condensed wurtzite-type Be<sub>2</sub>PN<sub>3</sub>.<sup>[35]</sup> Consequently, we have adapted this method for the reaction of Be<sub>3</sub>N<sub>2</sub> and Ge<sub>3</sub>N<sub>4</sub>.

In this contribution, we report on the discovery and bulk synthesis of BeGeN<sub>2</sub>, which crystallizes in a unique structure. In addition, a comprehensive comparison to its lighter homologue BeSiN<sub>2</sub> 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<sub>3</sub>N<sub>2</sub> and Ge<sub>3</sub>N<sub>4</sub> according to Equation 1.



The starting materials and 2 % NH<sub>4</sub>N<sub>3</sub> 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 Ge<sub>3</sub>N<sub>4</sub> at the reaction conditions. Consequently, the sample was washed with a 1:1 vol % mixture of concentrated NaOH with 30 % H<sub>2</sub>O<sub>2</sub> to remove Ge. The washed, colorless sample consists of crystals with a size up to 5 μm in length, as shown in Figure S1. EDX analysis detected no other elements than Ge, N and small amounts of O. Detailed information on the HP/HT synthesis of BeGeN<sub>2</sub> can be found in the Supporting Information.

For the comparison of the properties of BeGeN<sub>2</sub> with its lighter homologue, BeSiN<sub>2</sub> was synthesized according to Equation 2 by the reaction of Be<sub>3</sub>N<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> at 1900 °C in

a radio-frequency furnace and was obtained in the form of plate-like crystals up to 40 μm length (Figure S1).<sup>[10]</sup> More information on the synthesis of BeSiN<sub>2</sub> can be found in the Supporting Information.

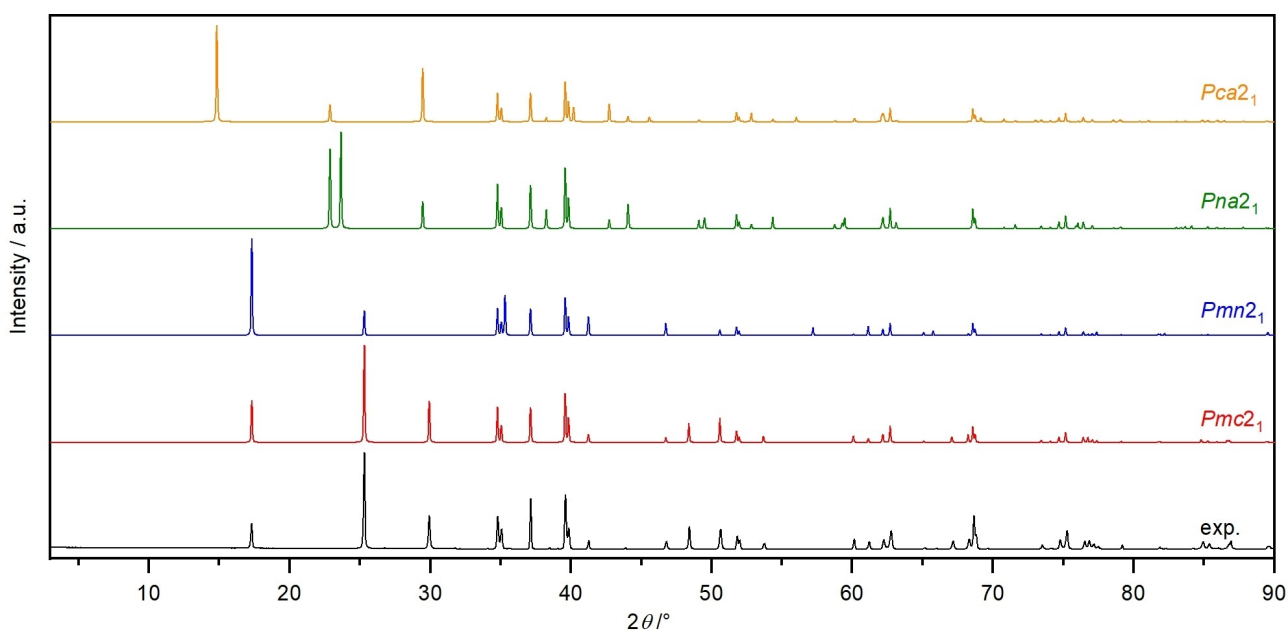


Due to the small crystal size, the structure of BeGeN<sub>2</sub> was elucidated from powder X-ray diffraction (PXRD) data by using the Charge Flipping method and subsequent Rietveld refinement (*Pmc*2<sub>1</sub> (no. 26),  $a=2.98324(5)$ ,  $b=5.11633(8)$ ,  $c=4.83927(8)$  Å,  $Z=2$ , Figure S3, more details in the Supporting Information).<sup>[36]</sup> As already shown, four different space groups are possible for the arrangement of the tetrahedra in a wurtzite-type II–IV–N<sub>2</sub> compound, namely *Pca*2<sub>1</sub>, *Pna*2<sub>1</sub>, *Pmn*2<sub>1</sub> and *Pmc*2<sub>1</sub> (see Figure S4). By comparing the theoretical diffraction patterns with the experimental one, it becomes clear, that BeGeN<sub>2</sub> crystallizes in space group *Pmc*2<sub>1</sub> (Figure 1). 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 2 and 3. The structure consists of regular BeN<sub>4</sub> (green) and GeN<sub>4</sub> (brown) tetrahedra that are connected in all vertices. Due to the overall four-fold coordination of both Be and Ge, BeGeN<sub>2</sub> should be categorized as a double nitride rather than a beryllium nitridogermanate.<sup>[37]</sup> 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 {3<sup>24</sup>.4<sup>33</sup>.5<sup>9</sup>} matches the one of analogous wurtzite.<sup>[38]</sup>

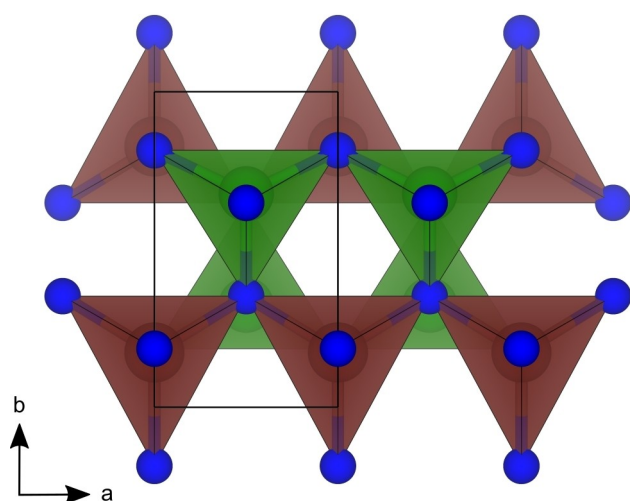
Distances and angles of Be–N (1.73583(5)–1.77883(6) Å; 105.4172(13)–118.255(3)°) and Ge–N tetrahedra (1.86326(5)–1.91648(7) Å; 106.186(3)–111.7844(14)°) are consistent with those in phenakite-type BeP<sub>2</sub>N<sub>4</sub> (Be–N: 1.720(4)–1.754(4) Å; 106.7(2)–115.1(3)°),<sup>[39]</sup>  $\alpha$ -Be<sub>3</sub>N<sub>2</sub> (Be–N: 1.731(11)–1.816(11) Å; 101.9(5)–120.9(5)°),<sup>[40]</sup> and MgGeN<sub>2</sub> (Ge–N: 1.803(15)–2.089(15) Å; 104.3(6)–114.3(7)°).<sup>[6]</sup>

The comparison of the structures of BeSiN<sub>2</sub> and BeGeN<sub>2</sub> raises the question of why BeGeN<sub>2</sub> crystallizes in space group *Pmc*2<sub>1</sub> and not *Pna*2<sub>1</sub>. Considering the ratio of ionic radii it becomes clear, that BeGeN<sub>2</sub> comprises a unique combination of two cations, namely Be<sup>2+</sup> (0.27 Å) and Ge<sup>4+</sup> (0.39 Å) with a radius ratio of 0.69 (Table S7).<sup>[28]</sup> More common combinations, e.g. MgGeN<sub>2</sub> or ZnSnN<sub>2</sub> 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.

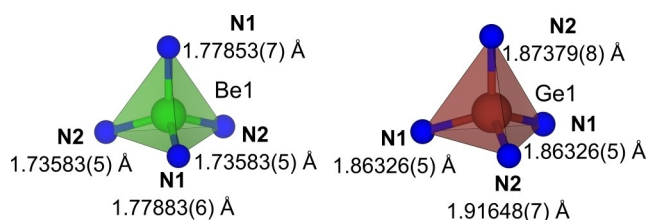
The calculation of the Madelung Part of the Lattice Energy (MAPLE) of BeGeN<sub>2</sub> (69999 kJ mol<sup>-1</sup>) is in very good agreement with the sum of the MAPLE values of formally constituting Be<sub>3</sub>N<sub>2</sub> and Ge<sub>3</sub>N<sub>4</sub> (70244 kJ mol<sup>-1</sup>, 0.4 % difference).<sup>[41]</sup> 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



**Figure 1.** Experimental powder diffraction pattern of  $\text{BeGeN}_2$  (black) as well as the simulated diffraction patterns for all theoretically possible four space groups for  $\text{BeGeN}_2$  derived from the wurtzite-type:  $Pmc2_1$  (red),  $Pmn2_1$  (blue),  $Pna2_1$  ( $\beta$ - $\text{NaFeO}_2$ -type, green), and  $Pca2_1$  (orange).



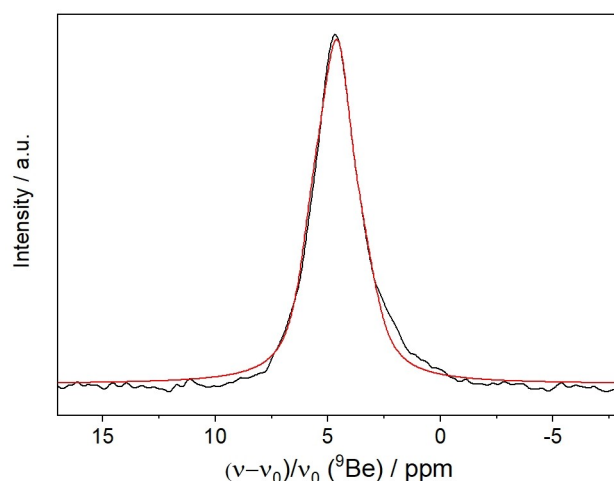
**Figure 2.** The crystal structure of  $\text{BeGeN}_2$  consists of all-side corner-sharing  $\text{BeN}_4$  (green) and  $\text{GeN}_4$  (brown) tetrahedra (N: blue). Viewed along [001] the wurtzite-type structure becomes apparent.



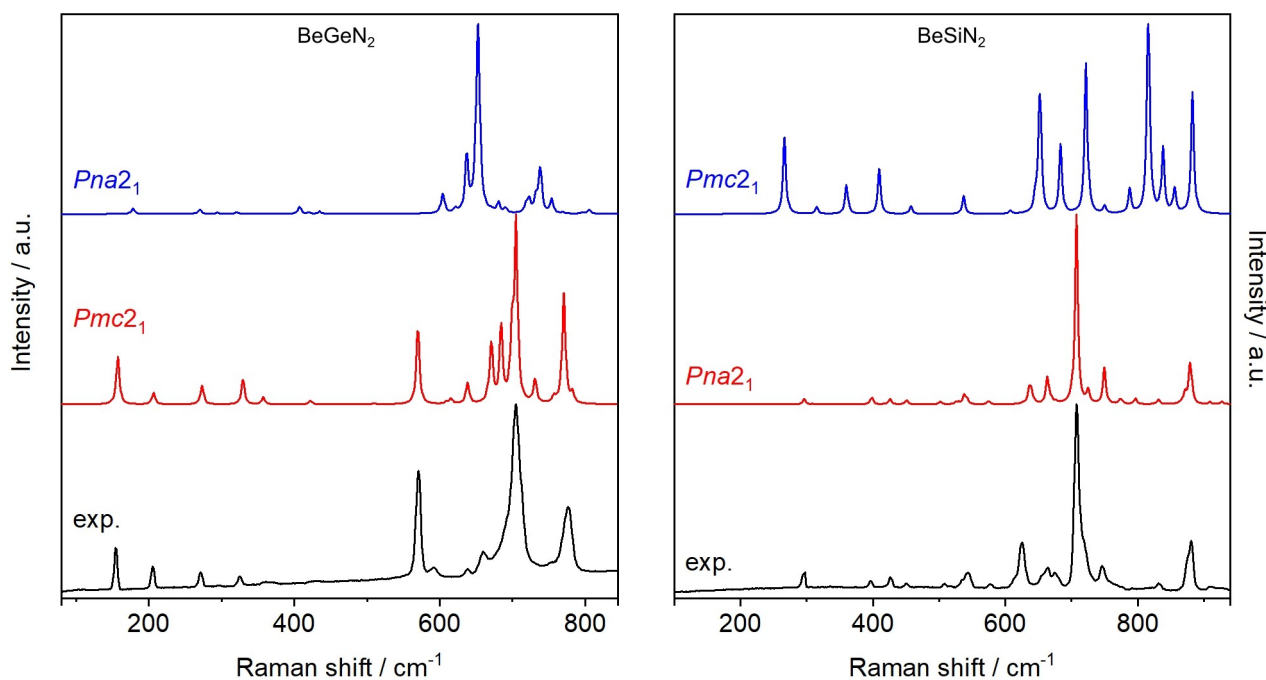
**Figure 3.** Coordination polyhedra of Be1 and Ge1.

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,  $^9\text{Be}$  MAS NMR experiments were performed with washed  $\text{BeGeN}_2$ . The  $^9\text{Be}$  spectrum (Figure 4) shows a single central-transition resonance around 4.7 ppm, compatible with one crystallographic site in  $\text{BeGeN}_2$  (2b). For the evaluation of this signal, quadrupolar interactions have to be taken into account ( $I(^9\text{Be}) = 3/2$ ). Analysis with the program DMFIT returns a quadrupolar coupling constant of  $C_q = 0.49$  MHz and an isotropic chemical shift of  $\delta_{\text{iso}} = 6.1$  ppm.<sup>[42]</sup> The magnitude of  $C_q$  is thus in the range expected for a homonuclear, but slightly distorted tetrahedral coordination of the Be atoms.<sup>[43]</sup> The value for  $\delta_{\text{iso}}$  is in good agreement



**Figure 4.**  $^9\text{Be}$  MAS NMR spectrum of  $\text{BeGeN}_2$  showing a single central-transition resonance around 4.7 ppm with experimental data (black) and fitting results (red).



**Figure 5.** Experimental Raman spectra (black) of BeGeN<sub>2</sub> (left) and BeSiN<sub>2</sub> (right) and the corresponding theoretical spectra for the space groups *Pna2*<sub>1</sub> ( $\beta$ -NaFeO<sub>2</sub>-type) and *Pmc2*<sub>1</sub>, 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.

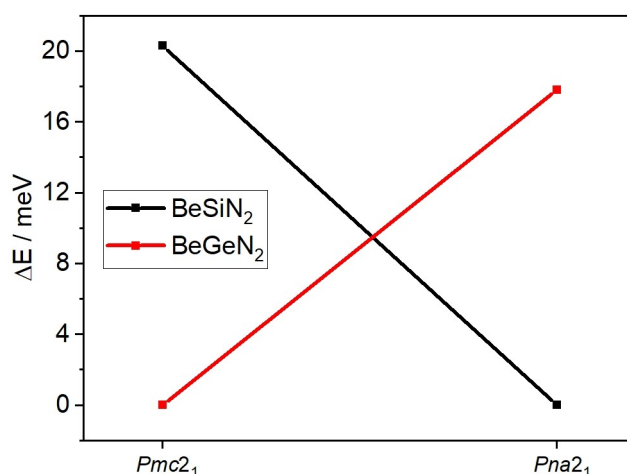
with Be<sub>3</sub>N<sub>2</sub> ( $\delta_{\text{iso}}=5.3$  ppm)<sup>[35]</sup> and BeSiN<sub>2</sub> ( $\delta_{\text{iso}}=5.5$  ppm,  $C_q=0.57$  MHz, Figure S5), which we determined in the same way. Hence, it can be assumed that the small oxygen content detected in the EDX spectra is likely to 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.

Although the comparison of the diffraction pattern of BeGeN<sub>2</sub> with the theoretical ones (Figure 1) and the corresponding Rietveld refinement (Figure S3) is sufficient to determine the unique structure, we tested the hypothesis, that the  $\beta$ -NaFeO<sub>2</sub> modification can be distinguished from the structure in the *Pmc2*<sub>1</sub> space group solely on the basis of Raman spectroscopy.<sup>[27]</sup> The differences in the spectra, displayed in Figure 5 become clearly apparent: For BeGeN<sub>2</sub> the experimental spectrum matches the calculated one for space group *Pmc2*<sub>1</sub> while the spectrum calculated for the *Pna2*<sub>1</sub> modification does not. For BeSiN<sub>2</sub> it is vice versa. Hence, the Raman spectrum confirms the presented structural model of BeGeN<sub>2</sub>. Moreover, future identification of thin film BeGeN<sub>2</sub>-type compounds could be feasible as stated by DFT calculations before.<sup>[27]</sup>

Second harmonic generation (SHG) effects were examined for both compounds, confirming non-centrosymmetric space groups. The SHG signal for BeGeN<sub>2</sub> is comparable to the one of quartz (Table S11). More details on SHG measurements and calculations can be found in the Supporting Information.

DFT calculations for BeGeN<sub>2</sub> and BeSiN<sub>2</sub> in all four possible space groups show that the two space groups *Pmn2*<sub>1</sub> and *Pca2*<sub>1</sub> are less stable (Figure S6). This is to be expected,

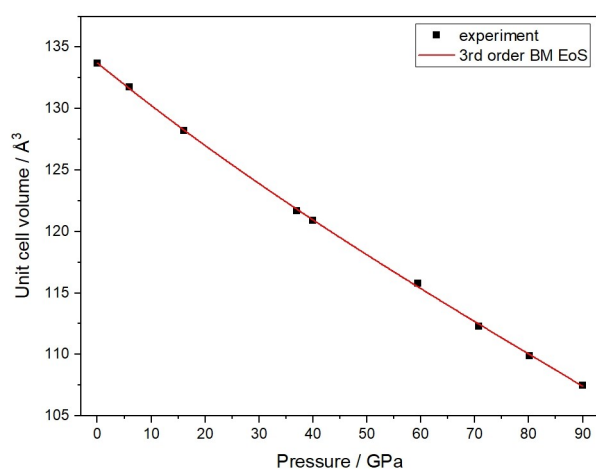
as the structures in these modifications do not obey the octet rule of local charge neutrality, as already discussed elsewhere.<sup>[23–24]</sup> For BeGeN<sub>2</sub>, the arrangement in *Pmc2*<sub>1</sub> is the most stable type with a difference of 18 meV ( $\sim 1.7$  kJ mol<sup>-1</sup>) to the  $\beta$ -NaFeO<sub>2</sub>-type (*Pna2*<sub>1</sub>). For BeSiN<sub>2</sub> it is vice versa with a difference of 20 meV ( $\sim 1.9$  kJ mol<sup>-1</sup>, Figure 6). The calculations are in line with our experimental results and in the same order of magnitude as DFT calculations on ZnSnN<sub>2</sub> disclosing a difference of 13 meV



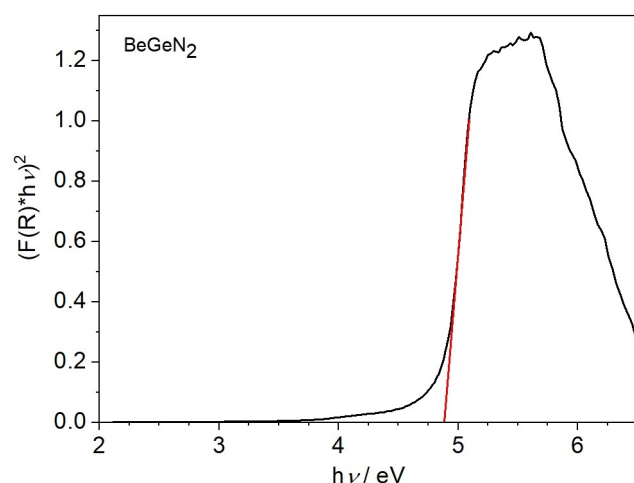
**Figure 6.** Results of DFT calculations of BeSiN<sub>2</sub> and BeGeN<sub>2</sub> for possible wurtzite-type structures in *Pmc2*<sub>1</sub> and *Pna2*<sub>1</sub>, confirming the experimental results.

between the  $\beta$ - $\text{NaFeO}_2$  ground state and the crystal structure in space group  $Pmc2_1$ .<sup>[26]</sup> More information on DFT calculations can be found in the Supporting Information.

The small energy differences between the different structure types arise the question, if phase transitions between them are possible. High-temperature PXRD for  $\text{BeGeN}_2$  shows that the compound is stable up to 800 °C (Figure S7). Beyond this point it starts decomposing forming elemental Ge.  $\text{BeSiN}_2$  stays stable at least until 900 °C (Figure S9) 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.<sup>[44]</sup> We intensively investigated the high-pressure behavior of  $\text{BeSiN}_2$  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



**Figure 7.** Pressure-volume data from pressure-dependent single crystal refinements of  $\text{BeSiN}_2$  were fitted with a 3<sup>rd</sup> order Birch-Murnaghan equation of state.



**Figure 8.** Tauc plot for a sample of  $\text{BeGeN}_2$  (black) with a tangent at the inflection point (red).

cell. However, the evaluation of experimental pressure-volume data reveals a bulk modulus  $K$  of 374(5) GPa (Figure 7,  $K' = 1.53(10)$ ), which identifies  $\text{BeSiN}_2$  as an ultra-incompressible material, far exceeding the calculated values of 220–263 GPa.<sup>[29,33, 45]</sup> More information on the DAC experiments and a discussion of the elastic properties of  $\text{BeSiN}_2$  can be found in the Supporting Information.

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 8 and S13).<sup>[46–47]</sup> The optical band gaps were determined to ~4.9 eV for  $\text{BeGeN}_2$  and ~4.5 eV for  $\text{BeSiN}_2$ , assuming a direct band gap. The results are consistent with DFT calculations from the literature (Table S14). However, they are contrary to the trend of decreasing band gap energies towards the heavier homologue, as can be observed, for example, in  $\text{MgMN}_2$  ( $M = \text{Si}$ : 4.8 eV;  $\text{Ge}$ : 3.2 eV) or  $\text{ZnMN}_2$  ( $M = \text{Si}$ : 3.7 eV;  $\text{Ge}$ : 3.2 eV).<sup>[6,11]</sup> 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.

Recently, we have reported on the synthesis of II–IV–N<sub>2</sub> (II = Mg, Mn, Zn; IV = Si, Ge) and their solid solutions, raising the question of the existence of the light homologue  $\text{BeGeN}_2$ .<sup>[6,11, 48]</sup> Now, it was synthesized in a high-pressure high-temperature approach starting from the binary nitrides  $\text{Be}_3\text{N}_2$  and  $\text{Ge}_3\text{N}_4$ . The compound crystallizes in a wurtzite-type structure in space group  $Pmc2_1$ , which has not been observed for any II–IV–N<sub>2</sub> 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  $\text{BeGeN}_2$  decomposes at temperatures higher than 800 °C,  $\text{BeSiN}_2$ , which was also investigated, shows neither a phase transition to the  $Pmc2_1$  space group at higher temperature or higher pressure up to 90 GPa, nor any other phase transition, but an elastic module  $K > 300$  GPa was elucidated. Optical band gaps of both materials were measured with UV/Vis spectroscopy. Further studies on Be–IV–V<sub>2</sub> 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 Be-containing compounds with wurtzite-type structure.

Although,  $\text{BeGeN}_2$  is the first wurtzite-type material crystallizing in the space group  $Pmc2_1$  and more research will be needed to explore all properties of this new compound, a bulk usage of  $\text{BeGeN}_2$  seems to be unfavorable due to serious safety concerns (see Supporting Information). However, the use of even small amounts of  $\text{BeGeN}_2$  could give access to other II–IV–N<sub>2</sub> compounds in space group  $Pmc2_1$ : A thin film of just a few layers of  $\text{BeGeN}_2$  could be grown, for example via chemical vapor deposition from  $\text{BeCl}_2$  and  $\text{GeCl}_4$  in  $\text{NH}_3$  or suitable single crystals could be synthesized under amonothermal conditions in an auto-

clave. 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 BeGeN<sub>2</sub>, other compounds might be grown on epitaxially. Possible examples may be ZnGeN<sub>2</sub> or ZnSnN<sub>2</sub> via vapor-phase epitaxy out of volatile ZnCl<sub>2</sub>, SnCl<sub>4</sub> in NH<sub>3</sub>, via metalorganic precursors or molecular beam epitaxy.<sup>[49–51]</sup> This synthesizing route could pave the way to the bulk synthesis of other BeGeN<sub>2</sub>-type nitride semiconductors.

### Supporting Information

The authors have cited additional references within the Supporting Information.<sup>[52–93]</sup>

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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