

Nitride Spinel: An Ultraincompressible High-Pressure Form of  $\text{BeP}_2\text{N}_4$ 

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Dedicated to Dr. Klaus Römer on the occasion of his 80th birthday

**Abstract:** Owing to its outstanding elastic properties, the nitride spinel  $\gamma\text{-Si}_3\text{N}_4$  is of considered interest for materials scientists and chemists. DFT calculations suggest that  $\text{Si}_3\text{N}_4$ -analog beryllium phosphorus nitride  $\text{BeP}_2\text{N}_4$  adopts the spinel structure at elevated pressures as well and shows outstanding elastic properties. Herein, we investigate phenakite-type  $\text{BeP}_2\text{N}_4$  by single-crystal synchrotron X-ray diffraction and report the phase transition into the spinel-type phase at 47 GPa and 1800 K in a laser-heated diamond anvil cell. The structure of spinel-type  $\text{BeP}_2\text{N}_4$  was refined from pressure-dependent *in situ* synchrotron powder X-ray diffraction measurements down to ambient pressure, which proves spinel-type  $\text{BeP}_2\text{N}_4$  a quenchable and metastable phase at ambient conditions. Its isothermal bulk modulus was determined to 325(8) GPa from equation of state, which indicates that spinel-type  $\text{BeP}_2\text{N}_4$  is an ultraincompressible material.

**D**ue to a broad range of materials properties and applications, oxide spinels with the general formula  $\text{AB}_2\text{O}_4$  (A, B = metal ions) are an extensively investigated field of research and numerous compounds have been reported.<sup>[1]</sup> In contrast, only few representatives of nitride spinels ( $\text{AB}_2\text{N}_4$ ) have been prepared, as yet.<sup>[2]</sup> However, they have already been proven to compete with oxide materials for outstanding materials properties, especially with regard to mechanical resilience.<sup>[3]</sup>

The synthesis of the group 14 nitrides  $\gamma\text{-Si}_3\text{N}_4$ ,<sup>[3,4]</sup>  $\gamma\text{-Ge}_3\text{N}_4$ ,<sup>[5]</sup> and  $\text{Sn}_3\text{N}_4$ <sup>[6]</sup> heralded a new era of nitride chemistry, as these compounds represent the first nitride spinels.<sup>[2]</sup>  $\gamma\text{-Si}_3\text{N}_4$  has been prepared in diamond anvil cells (DAC),<sup>[3]</sup> multianvil presses,<sup>[4]</sup> as well as in shockwave experiments,<sup>[7]</sup> and recently even the preparation of macroscopic transparent polycrystalline  $\gamma\text{-Si}_3\text{N}_4$  windows has been achieved.<sup>[8]</sup> The isothermal bulk modulus  $K_0$  and the Vickers hardness  $H_V$  of  $\gamma\text{-Si}_3\text{N}_4$  have been determined to  $K_0 = 290\text{--}317$  GPa<sup>[3,8–10]</sup> and  $H_V = 30\text{--}43$  GPa,<sup>[8,10–12]</sup> which makes it one of the most incompressible and hardest low-density materials.

Due to the topological rigidity of spinels, they are considered to intrinsically feature outstanding elastic properties, which might be further enhanced by strong covalent A–N and B–N bonds in the case of nitride spinels.<sup>[13–16]</sup> The elemental diversity of nitride spinels, however, is comparatively small, as experimental and theoretical research on nitride spinels has most widely been limited to the binary and ternary nitrides of C, Si, Ge, Sn, Pb, Ti, and Zr,<sup>[16–19]</sup> and only nitride spinels of tetravalent cations ( $\text{A}^{\text{IV}}$ ,  $\text{B}^{\text{IV}} = \text{Si, Ge, Sn}$ ) have been prepared, as yet.<sup>[3,5,6,20]</sup>

Besides tetravalent cations, a nitride spinel with the general formula  $\text{AB}_2\text{N}_4$  may also be composed of  $\text{A}^{\text{VI}}$  and  $\text{B}^{\text{III}}$  ( $\text{A}^{\text{VI}}\text{B}^{\text{III}}_2\text{N}_4$ ) or  $\text{A}^{\text{II}}$  and  $\text{B}^{\text{V}}$  cations ( $\text{A}^{\text{II}}\text{B}^{\text{V}}_2\text{N}_4$ ), when electrostatic neutrality is stipulated. The II–V combination has been reported for several phosphorus(V) nitride materials with the general formula  $\text{M}^{\text{II}}\text{P}_2\text{N}_4$  ( $\text{M}^{\text{II}} = \text{Be, Ca, Sr, Ba, Mn, Cd}$ ), which form  $\text{PN}_4$  tetrahedra based networks.<sup>[21,22]</sup> To the best of our knowledge, a spinel-type phase, however, has not been reported for any  $\text{A}^{\text{VI}}\text{B}^{\text{III}}_2\text{N}_4$  or  $\text{A}^{\text{II}}\text{B}^{\text{V}}_2\text{N}_4$ , as yet.

Theoretical investigations have predicted spinel-type (sp)  $\text{BeP}_2\text{N}_4$  as a stable polymorph at elevated pressures, which makes it a promising candidate for the first  $\text{A}^{\text{II}}\text{B}^{\text{V}}_2\text{N}_4$ -type nitride spinel.<sup>[21,23–25]</sup> Hitherto, only phenakite-type (phe)  $\text{BeP}_2\text{N}_4$  has been reported, which is isoelectronic and homeotypic with  $\beta\text{-Si}_3\text{N}_4$  and features  $\text{BeN}_4$  and  $\text{PN}_4$  tetrahedra.<sup>[21,26,27]</sup> By analogy with the  $\text{Si}_3\text{N}_4$  polymorphism, phe- $\text{BeP}_2\text{N}_4$  is considered to undergo a phase transition into the regular spinel structure with Be and P occupying tetrahedral and octahedral voids of the cubic close-packing of N, respectively.<sup>[21]</sup>  $\text{BeN}_4$  tetrahedra are a common motif in crystal chemistry of beryllium nitrides,<sup>[28]</sup> whereas  $\text{PN}_6$  octahedra have only been reported in the high-pressure polymorph  $\beta\text{-BP}_3\text{N}_6$ , recently.<sup>[29]</sup>

The phenakite- to spinel-type transition pressure of  $\text{BeP}_2\text{N}_4$  has been predicted to 14–24 GPa from DFT calculations and due to its covalent character, sp- $\text{BeP}_2\text{N}_4$ <sup>[30]</sup> is suggested to be quenchable to ambient pressure as a meta-

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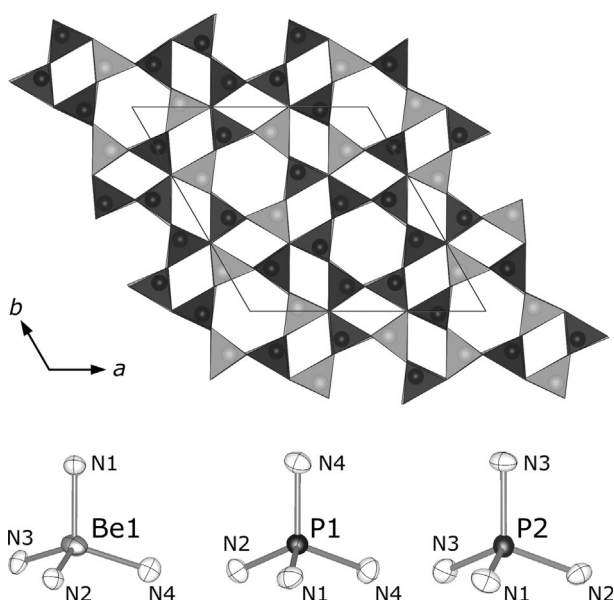
stable phase.<sup>[21,23,24]</sup> Its isothermal bulk modulus has been calculated to be in the range of 263–291 GPa, which emphasizes the kinship with  $\gamma$ -Si<sub>3</sub>N<sub>4</sub>.<sup>[21,23–25]</sup> Moreover, the Vickers hardness  $H_V$  of sp-BeP<sub>2</sub>N<sub>4</sub> has been estimated to approximately  $H_V = 45$  GPa using (semi-)empirical approaches, which would make it a promising candidate for a superhard low-density material.<sup>[24,31]</sup>

Herein, we report on the phe-BeP<sub>2</sub>N<sub>4</sub> → sp-BeP<sub>2</sub>N<sub>4</sub> phase transition at 47 GPa, which was investigated in a laser-heated DAC employing in situ synchrotron X-ray diffraction (XRD) measurements. The structure of sp-BeP<sub>2</sub>N<sub>4</sub> was refined using the Rietveld method and its elastic properties have been investigated upon cold decompression to ambient pressure.

phe-BeP<sub>2</sub>N<sub>4</sub> was initially synthesized from Be<sub>3</sub>N<sub>2</sub> and P<sub>3</sub>N<sub>5</sub> in a large volume press at 7 GPa and 1500 °C, employing the multianvil technique [Eq. (1), more details are provided in the Supporting Information].<sup>[21]</sup>



To select a suitable particle for in situ high-pressure investigations and to verify the phenakite-type structure of BeP<sub>2</sub>N<sub>4</sub>, several polycrystalline grains were screened by synchrotron XRD measurements at ambient conditions (Supporting Information, Figure S2). Integration of the most intense domain of a multi-domain crystalline grain yielded a suitable single-crystal data set (Figure S3), from which the structure of phe-BeP<sub>2</sub>N<sub>4</sub> was elucidated ( $R\bar{3}$  (no. 148),  $a = 12.6979(15)$ ,  $c = 8.3595(10)$  Å,  $V = 1167.3(5)$  Å<sup>3</sup>,  $Z = 18$ ). All atoms were refined with anisotropic displacement parameters and the mean interatomic Be–N and P–N distances are 1.734(15) and 1.636(8) Å, respectively, which is in line with values that have been reported for the binary nitrides.<sup>[28,32]</sup> The here obtained structural model verifies the model previously reported by Pucher et al. that has been



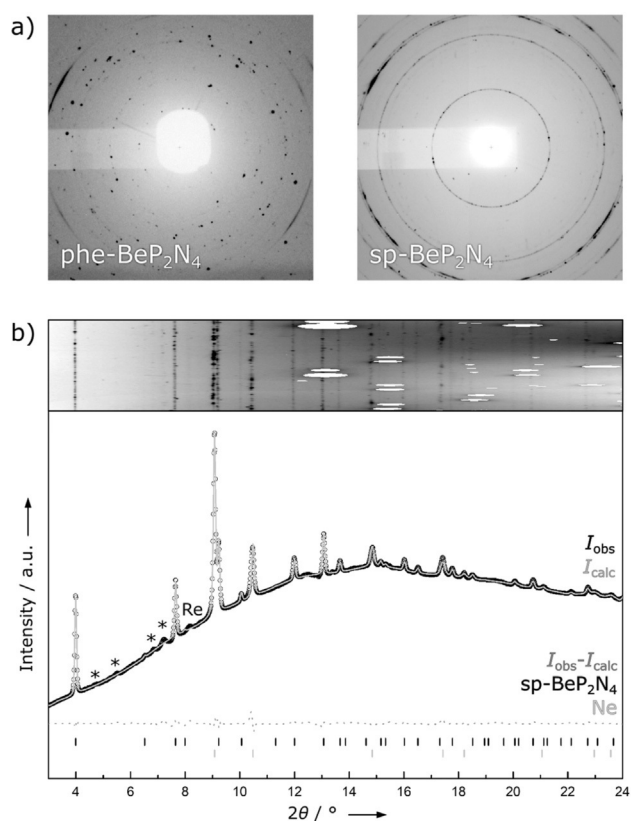
**Figure 1.** Crystal structure of phe-BeP<sub>2</sub>N<sub>4</sub> as obtained from single-crystal synchrotron XRD. Be (gray) and P (black) are in fourfold N-coordination and ellipsoids are displayed at 99% probability level.

solved and refined from powder XRD data (Tables S4 and S7).<sup>[21,33]</sup> Figure 1 illustrates the single-crystal structure of phe-BeP<sub>2</sub>N<sub>4</sub> as well as the constituting BeN<sub>4</sub> and PN<sub>4</sub> tetrahedra. More detailed information on the synchrotron XRD measurement and the structure refinement of phe-BeP<sub>2</sub>N<sub>4</sub> is provided in the Supporting Information (Tables S4–S7).

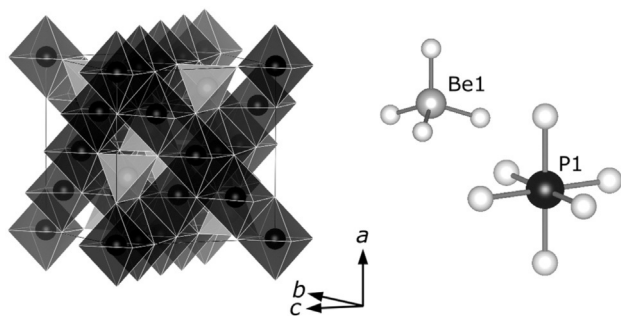
To investigate the predicted phe-BeP<sub>2</sub>N<sub>4</sub> → sp-BeP<sub>2</sub>N<sub>4</sub> phase transition, the pre-selected particle of phe-BeP<sub>2</sub>N<sub>4</sub> was loaded in a DAC with Ne serving as a pressure transmitting medium and ruby as an internal pressure standard. The sample was cold-compressed in two steps to a maximum pressure of 47.3(9) GPa. At both steps a XRD step scan was collected that could be indexed with the metrics of phe-BeP<sub>2</sub>N<sub>4</sub> (Figure S8, Table S9). Owing to very low intensities, a refinement of the integrated data, however, was not feasible at those pressures. At 47.3(9) GPa the unit cell of phe-BeP<sub>2</sub>N<sub>4</sub> has contracted by approximately 16 vol% in comparison to the ambient pressure model (Figure S11).

To induce the phase transition into the spinel-type structure, the phe-BeP<sub>2</sub>N<sub>4</sub> particle was laser-heated from both sides to an average temperature of 1800(200) K at 47.3(9) GPa (NIR fiber laser ( $\lambda = 1070$  nm)). This pressure was deemed sufficient for the formation of PN<sub>6</sub> octahedra, as this motif was recently proven at 42 GPa in  $\beta$ -BP<sub>3</sub>N<sub>6</sub>.<sup>[29]</sup> The sample was monitored with in situ synchrotron XRD scans for the course of the heating period. After a few seconds, unidentified Bragg reflections appeared and heating for another minute led to an almost full conversion of phe-BeP<sub>2</sub>N<sub>4</sub> (Figure 2 and S10). Subsequently, the sample was allowed to cool down to ambient temperature, after which a XRD wide scan was collected. The powder XRD pattern of the new phase matched the Bragg reflections of the predicted spinel-type phase (Figures 2 and S10).<sup>[21]</sup> Therefore, the experimental pressure of about 47 GPa is proven sufficiently high for the phe-BeP<sub>2</sub>N<sub>4</sub> → sp-BeP<sub>2</sub>N<sub>4</sub> phase transition, but the minimum transition pressure may be most likely significantly lower, considering theoretical investigations on sp-BeP<sub>2</sub>N<sub>4</sub> ( $p_{\text{trans}} = 14$ – $24$  GPa)<sup>[21,24]</sup> and experimental examinations of isoelectronic  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> ( $p_{\text{trans}} \approx 13$  GPa).<sup>[3,4,9]</sup>

Single-crystal XRD measurements of sp-BeP<sub>2</sub>N<sub>4</sub> were not feasible, as the title compound did not form any adequate domains (Figure 2 a). Therefore, the sp-BeP<sub>2</sub>N<sub>4</sub> structure was refined on PXRD data obtained at 47.3(9) GPa employing the Rietveld method (Table S12).<sup>[34]</sup> The DFT-based model was used as a starting point for the refinement and was subsequently corroborated by the experimental data.<sup>[21]</sup> sp-BeP<sub>2</sub>N<sub>4</sub> crystallizes in the regular spinel structure ( $Fd\bar{3}m$ , no. 227,  $a = 7.1948(2)$  Å,  $V = 372.44(3)$  Å<sup>3</sup>,  $Z = 8$ ) with site symmetries Be( $8b, \bar{4}3m$ ), P( $16c, \bar{3}m$ ), and N( $32e, .3m$ ).<sup>[21,35]</sup> More detailed information on the structure refinement is provided in the Supporting Information (Tables S12 and S14–S16, Figure S13). No experimental evidence for Be/P disorder or an inverse spinel structure was observed. This is in agreement with the calculations presented by Pucher et al. that characterized the inverse spinel-type BeP<sub>2</sub>N<sub>4</sub> to be unfavored towards phe- and sp-BeP<sub>2</sub>N<sub>4</sub>.<sup>[21]</sup> The refined crystal structure of sp-BeP<sub>2</sub>N<sub>4</sub> and the respective coordination polyhedra of Be and P are illustrated in Figure 3. The interatomic Be–N and



**Figure 2.** (a) XRD scans of the  $\text{BeP}_2\text{N}_4$  sample before (left) and after laser heating at 47.3(9) GPa (right), corresponding to phe- and sp- $\text{BeP}_2\text{N}_4$ , respectively. (b) Rietveld refinement of sp- $\text{BeP}_2\text{N}_4$  and Ne at 47.3(9) GPa from in situ X-ray measurements using synchrotron radiation ( $\lambda = 0.2894 \text{ \AA}$ ). Observed and calculated XRD intensities: black circles, gray line; difference plot: dotted gray line; positions of Bragg reflections of sp- $\text{BeP}_2\text{N}_4$  and Ne: black and gray vertical bars. Reflections of minor residues of phe- $\text{BeP}_2\text{N}_4$  are marked by asterisks and weak scattering of the Re gasket is labelled.<sup>[21]</sup>



**Figure 3.** The crystal structure of sp- $\text{BeP}_2\text{N}_4$  as refined from PXRD data collected at 47.3(9) GPa. Be (gray) occupies tetrahedral and P (black) octahedral voids in a cubic close-packing of N (white), corresponding to the regular spinel structure.

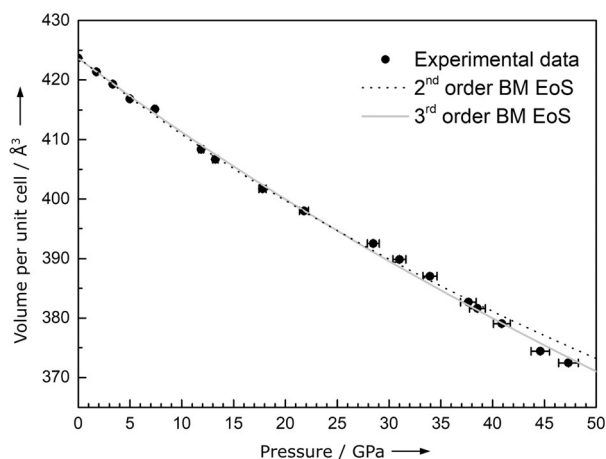
P–N distances at 47.3(9) GPa are 1.635(2) and 1.755(2)  $\text{\AA}$ , respectively, corresponding to fourfold coordinated Be and sixfold coordinated P.

To verify the sp- $\text{BeP}_2\text{N}_4$  structure in terms of electrostatics, the Madelung part of lattice energy (MAPLE) was

analyzed.<sup>[36]</sup> The calculated MAPLE value of sp- $\text{BeP}_2\text{N}_4$  is 58140  $\text{kJ mol}^{-1}$ , which is in very good agreement with the values calculated for phe- $\text{BeP}_2\text{N}_4$  (58542  $\text{kJ mol}^{-1}$ ,  $\Delta E = 0.7\%$ ) and the weighted sum of the binary nitrides  $\text{P}_3\text{N}_5$  and  $\text{Be}_3\text{N}_2$  (58992  $\text{kJ mol}^{-1}$ ,  $\Delta E = 1.4\%$ ). More detailed information on MAPLE calculations are provided in Table S19.

Incremental cold decompression of sp- $\text{BeP}_2\text{N}_4$  to ambient pressure was monitored by in situ PXRD measurements at 17 pressure points (Figure S11, Table S16). The pressure-dependent Rietveld refinements show that sp- $\text{BeP}_2\text{N}_4$  is quenchable to ambient conditions. The expansion of the unit cell upon decompression from 47.3(9) GPa to ambient pressure was 14 vol %, while the interatomic Be–N and P–N distances at ambient pressure expanded to 1.752(2) and 1.808(2)  $\text{\AA}$ , respectively (Table S16, Figure S17). These values are in good agreement with values from the DFT model and with those reported for  $\text{BeN}_4$  and  $\text{PN}_6$  polyhedra in  $\text{Be}_3\text{N}_2$  and  $\beta\text{-BP}_3\text{N}_6$ .<sup>[21,28,29]</sup>

According to DFT calculations, sp- $\text{BeP}_2\text{N}_4$  is considered to show a very low compressibility ( $263 < K_0 < 291 \text{ GPa}$ ).<sup>[21,23–25]</sup> Thus, the pressure-volume data from pressure-dependent Rietveld refinements were fitted with both, a 2<sup>nd</sup> and a 3<sup>rd</sup> order Birch-Murnaghan (BM) equation of state (EoS), yielding the fitting parameters  $V_0 = 423.76(7) \text{ \AA}^3$ ,  $K_0 = 305(5) \text{ GPa}$ ,  $K_0' = 4$  (fixed) and  $V_0 = 423.68(6) \text{ \AA}^3$ ,  $K_0 = 325(8) \text{ GPa}$ ,  $K_0' = 2.4(5)$ , respectively (Figure 4, S20).<sup>[37]</sup> These findings render sp- $\text{BeP}_2\text{N}_4$  an ultraincompressible material,<sup>[13,38]</sup> exceeding the bulk modulus of  $\gamma\text{-Si}_3\text{N}_4$  as well as the predicted values from DFT calculations. Its hardness and thermal stability, however, have not been investigated experimentally, as yet. As the title compound is quenchable to ambient conditions and may form at significantly lower pressures, its synthesis may be reproduced in large volume presses, providing sample amounts suitable for future investigations in terms of its elastic, physical, and optical properties. More detailed information on the BM EoS fits and the elastic properties of sp- $\text{BeP}_2\text{N}_4$  is provided in the Supporting Information.



**Figure 4.** The pressure-volume data from pressure-dependent Rietveld refinements were fitted with a 2<sup>nd</sup> and 3<sup>rd</sup> order Birch-Murnaghan equation of state (BM EoS), with fitting parameters provided in the main text. The isothermal bulk modulus of > 300 GPa renders sp- $\text{BeP}_2\text{N}_4$  an ultraincompressible material.<sup>[13]</sup>

Recapitulating, phe-BeP<sub>2</sub>N<sub>4</sub> was synthesized in a high-pressure high-temperature reaction and the literature-known structure model was confirmed by single-crystal synchrotron XRD measurements. As predicted from theoretical studies, phe-BeP<sub>2</sub>N<sub>4</sub> was transformed into the spinel-type phase at 47 GPa and 1800 K using a laser-heated DAC. sp-BeP<sub>2</sub>N<sub>4</sub> was proven to be quenchable to ambient pressure and it is rendered an ultraincompressible material from equation of states. Therefore, the title compound is the first A<sup>II</sup>B<sup>V</sup>N<sub>4</sub>-type nitride spinel and a pioneer compound that extends the still narrow field of nitride spinels by introducing ions with oxidation states +II and +V. This should encourage further experimental investigations on mixed nitride spinels, as they appear as promising compounds for next-generation materials. Thus, future investigations may deal with the incorporation of divalent (e.g. Mg, Zn, Cu, Ni) and pentavalent cations (e.g. V, Nb, or Ta) into II-V nitride spinels, which might introduce intriguing optical and magnetic properties to this emerging field of research.

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### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** high-pressure chemistry · nitrides · solid-state structures · spinel · synchrotron radiation

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