High-Pressure Chemistry

Nitride Spinel: An Ultraincompressible High-Pressure Form of BeP₂N₄

*Sebastian Vogel, Maxim Bykov, Elena Bykova, Sebastian Wendl, Simon D. Kloß,
Anna Pakhomova, Natalia Dubrovinskaia, Leonid Dubrovinsky, and Wolfgang Schnick**

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

Abstract: *Owing to its outstanding elastic properties, the nitride spinel γ-Si₃N₄ is of considered interest for materials scientists and chemists. DFT calculations suggest that Si₃N₄-analog beryllium phosphorus nitride BeP₂N₄ adopts the spinel structure at elevated pressures as well and shows outstanding elastic properties. Herein, we investigate phenakite-type BeP₂N₄ 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 BeP₂N₄ was refined from pressure-dependent in situ synchrotron powder X-ray diffraction measurements down to ambient pressure, which proves spinel-type BeP₂N₄ 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 BeP₂N₄ is an ultraincompressible material.*

Due to a broad range of materials properties and applications, oxide spinels with the general formula AB_2O_4 (A, B = metal ions) are an extensively investigated field of research and numerous compounds have been reported.[1] In contrast, only few representatives of nitride spinels (AB_2N_4) have been prepared, as yet.[2] However, they have already been proven to compete with oxide materials for outstanding materials properties, especially with regard to mechanical resilience.[3]

[*] S. Vogel, Dr. M. Bykov, S. Wendl, Dr. S. D. Kloß, Prof. Dr. W. Schnick
Department of Chemistry, University of Munich (LMU)
Butenandtstraße 5–13, 81377 Munich (Germany)
E-mail: wolfgang.schnick@uni-muenchen.de

Dr. E. Bykova, Prof. Dr. L. Dubrovinsky
Bayerisches Geoinstitut (BGI), University of Bayreuth
95440 Bayreuth (Germany)

Dr. E. Bykova, Dr. A. Pakhomova
Deutsches Elektronen-Synchrotron (DESY)
22607 Hamburg (Germany)

Prof. Dr. N. Dubrovinskaia
Material Physics and Technology at Extreme Conditions
University of Bayreuth
95440 Bayreuth (Germany)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
https://doi.org/10.1002/anie.201910998.

The synthesis of the group 14 nitrides γ-Si₃N₄,[3,4] γ-Ge₃N₄,[5] and Sn₃N₄[6] heralded a new era of nitride chemistry, as these compounds represent the first nitride spinels.[2] γ-Si₃N₄ has been prepared in diamond anvil cells (DAC),[3] multianvil presses,[4] as well as in shockwave experiments,[7] and recently even the preparation of macroscopic transparent polycrystalline γ-Si₃N₄ windows has been achieved.[8] The isothermal bulk modulus K_0 and the Vickers hardness H_V of γ-Si₃N₄ have been determined to $K_0 = 290–317$ GPa[3,8–10] and $H_V = 30–43$ GPa,[8,10–12] 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.[13–16] 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,[16–19] and only nitride spinels of tetravalent cations (A^{IV}, B^{IV} = Si, Ge, Sn) have been prepared, as yet.[3,5,6,20]

Besides tetravalent cations, a nitride spinel with the general formula AB_2N_4 may also be composed of A^{VI} and B^{III} ($A^{VI}B^{III}_2N_4$) or A^{II} and B^V cations ($A^{II}B^V_2N_4$), when electrostatic neutrality is stipulated. The II–V combination has been reported for several phosphorus(V) nitride materials with the general formula $M^{II}P_2N_4$ (M^{II} = Be, Ca, Sr, Ba, Mn, Cd), which form PN_4 tetrahedra based networks.[21,22] To the best of our knowledge, a spinel-type phase, however, has not been reported for any $A^{VI}B^{III}_2N_4$ or $A^{II}B^V_2N_4$, as yet.

Theoretical investigations have predicted spinel-type (sp) BeP₂N₄ as a stable polymorph at elevated pressures, which makes it a promising candidate for the first $A^{II}B^V_2N_4$-type nitride spinel.[21,23–25] Hitherto, only phenakite-type (phe) BeP₂N₄ has been reported, which is isoelectronic and homeotypic with β-Si₃N₄ and features BeN₄ and PN₄ tetrahedra.[21,26,27] By analogy with the Si₃N₄ polymorphism, phe-BeP₂N₄ 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.[21] BeN₄ tetrahedra are a common motif in crystal chemistry of beryllium nitrides,[28] whereas PN₆ octahedra have only been reported in the high-pressure polymorph β-BP₃N₆, recently.[29]

The phenakite- to spinel-type transition pressure of BeP₂N₄ has been predicted to 14–24 GPa from DFT calculations and due to its covalent character, sp-BeP₂N₄[30] is suggested to be quenchable to ambient pressure as a meta-

stable phase.[21,23,24] Its isothermal bulk modulus has been calculated to be in the range of 263–291 GPa, which emphasizes the kinship with γ-Si$_3$N$_4$.[21,23–25] Moreover, the Vickers hardness H_V of sp-BeP$_2$N$_4$ 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.[24,31]

Herein, we report on the phe-BeP$_2$N$_4$→sp-BeP$_2$N$_4$ 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$_2$N$_4$ was refined using the Rietveld method and its elastic properties have been investigated upon cold decompression to ambient pressure.

phe-BeP$_2$N$_4$ was initially synthesized from Be$_3$N$_2$ and P$_3$N$_5$ 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].[21]

$$Be_3N_2 + 2\,P_3N_5 \rightarrow 3\,\text{phe-}BeP_2N_4 \tag{1}$$

To select a suitable particle for in situ high-pressure investigations and to verify the phenakite-type structure of BeP$_2$N$_4$, 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$_2$N$_4$ was elucidated ($R\bar{3}$ (no. 148), $a = 12.6979(15)$, $c = 8.3595(10)$ Å, $V = 1167.3(5)$ Å^3, $Z = 18$). 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.[28,32] The here obtained structural model verifies the model previously reported by Pucher et al. that has been
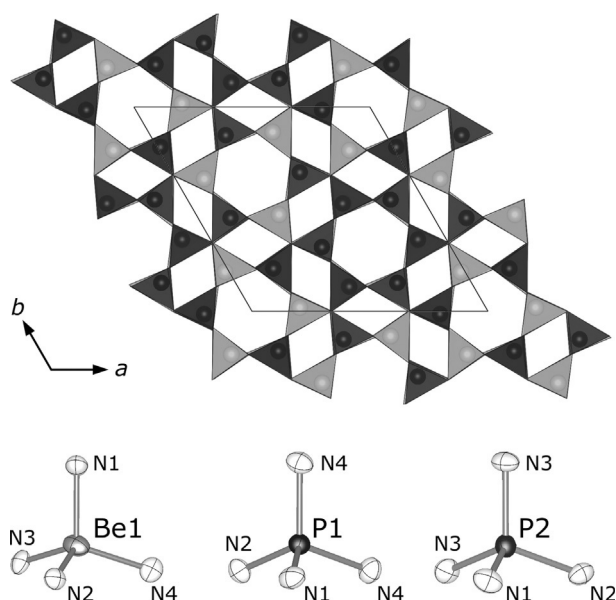

Figure 1. Crystal structure of phe-BeP$_2$N$_4$ as obtained from single-crystal synchrotron XRD. Be (gray) and P (black) are in fourfold N-coordination and ellipsoids are displayed at 99% probability level.

solved and refined from powder XRD data (Tables S4 and S7).[21,33] Figure 1 illustrates the single-crystal structure of phe-BeP$_2$N$_4$ as well as the constituting BeN$_4$ and PN$_4$ tetrahedra. More detailed information on the synchrotron XRD measurement and the structure refinement of phe-BeP$_2$N$_4$ is provided in the Supporting Information (Tables S4–S7).

To investigate the predicted phe-BeP$_2$N$_4$→sp-BeP$_2$N$_4$ phase transition, the pre-selected particle of phe-BeP$_2$N$_4$ 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$_2$N$_4$ (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$_2$N$_4$ 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$_2$N$_4$ 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$_6$ octahedra, as this motif was recently proven at 42 GPa in β-BP$_3$N$_6$.[29] 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$_2$N$_4$ (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).[21] Therefore, the experimental pressure of about 47 GPa is proven sufficiently high for the phe-BeP$_2$N$_4$→sp-BeP$_2$N$_4$ phase transition, but the minimum transition pressure may be most likely significantly lower, considering theoretical investigations on sp-BeP$_2$N$_4$ ($p_{trans} = 14$–24 GPa)[21,24] and experimental examinations of isoelectronic γ-Si$_3$N$_4$ ($p_{trans} \approx 13$ GPa).[3,4,9]

Single-crystal XRD measurements of sp-BeP$_2$N$_4$ were not feasible, as the title compound did not form any adequate domains (Figure 2a). Therefore, the sp-BeP$_2$N$_4$ structure was refined on PXRD data obtained at 47.3(9) GPa employing the Rietveld method (Table S12).[34] The DFT-based model was used as a starting point for the refinement and was subsequently corroborated by the experimental data.[21] sp-BeP$_2$N$_4$ crystallizes in the regular spinel structure ($Fd\bar{3}m$, no. 227, $a = 7.1948(2)$ Å, $V = 372.44(3)$ Å^3, $Z = 8$) with site symmetries Be(8b, $\bar{4}3m$), P(16c, $.\bar{3}m$), and N(32e, $.3m$).[21,35] 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$_2$N$_4$ to be unfavored towards phe- and sp-BeP$_2$N$_4$.[21] The refined crystal structure of sp-BeP$_2$N$_4$ and the respective coordination polyhedra of Be and P are illustrated in Figure 3. The interatomic Be–N and
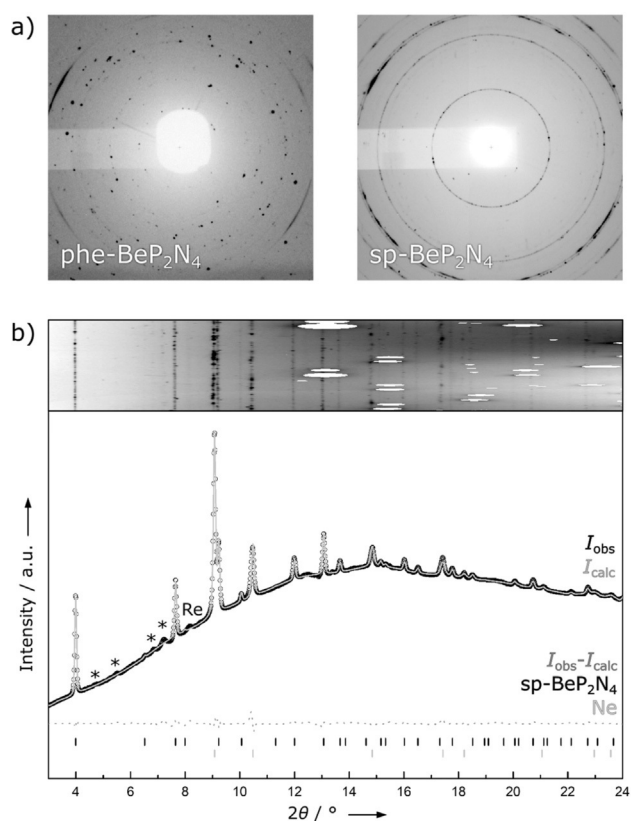
Figure 2. (a) XRD scans of the BeP_2N_4 sample before (left) and after laser heating at 47.3(9) GPa (right), corresponding to phe- and sp-BeP_2N_4, respectively. (b) Rietveld refinement of sp-BeP_2N_4 and Ne at 47.3(9) GPa from in situ X-ray measurements using synchrotron radiation ($\lambda = 0.2894$ Å). Observed and calculated XRD intensities: black circles, gray line; difference plot: dotted gray line; positions of Bragg reflections of sp-BeP_2N_4 and Ne: black and gray vertical bars. Reflections of minor residues of phe-BeP_2N_4 are marked by asterisks and weak scattering of the Re gasket is labelled.[21]
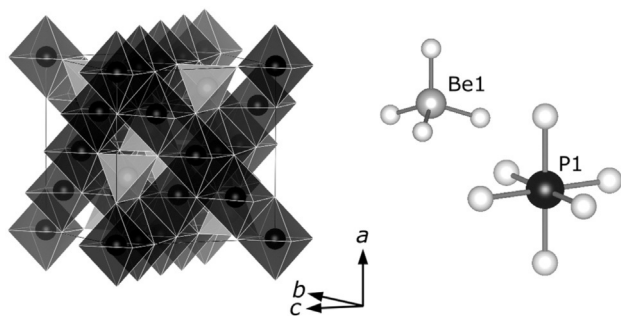

Figure 3. The crystal structure of sp-BeP_2N_4 as refined from PXRD data collected at 47.3(9) GPa. Be (gray) occupies tetrahedral and P (black) octahedral voids in a cubic close-packing of N (white), corresponding to the regular spinel structure.

P−N distances at 47.3(9) GPa are 1.635(2) and 1.755(2) Å, respectively, corresponding to fourfold coordinated Be and sixfold coordinated P.

To verify the sp-BeP_2N_4 structure in terms of electro-statics, the Madelung part of lattice energy (MAPLE) was

analyzed.[36] The calculated MAPLE value of sp-BeP_2N_4 is 58140 kJmol^{-1}, which is in very good agreement with the values calculated for phe-BeP_2N_4 (58542 kJmol^{-1}, $\Delta E = 0.7\%$) and the weighted sum of the binary nitrides P_3N_5 and Be_3N_2 (58992 kJmol^{-1}, $\Delta E = 1.4\%$). More detailed information on MAPLE calculations are provided in Table S19.

Incremental cold decompression of sp-BeP_2N_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-BeP_2N_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) Å, respectively (Table S16, Figure S17). These values are in good agreement with values from the DFT model and with those reported for BeN_4 and PN_6 polyhedra in Be_3N_2 and β-BP_3N_6.[21,28,29]

According to DFT calculations, sp-BeP_2N_4 is considered to show a very low compressibility ($263 < K_0 < 291$ GPa).[21,23–25] Thus, the pressure-volume data from pressure-dependent Rietveld refinements were fitted with both, a 2nd and a 3rd order Birch-Murnaghan (BM) equation of state (EoS), yielding the fitting parameters $V_0 = 423.76(7)$ Å^3, $K_0 = 305(5)$ GPa, $K_0' = 4$ (fixed) and $V_0 = 423.68(6)$ Å^3, $K_0 = 325$-(8) GPa, $K_0' = 2.4(5)$, respectively (Figure 4, S20).[37] These findings render sp-BeP_2N_4 an ultraincompressible mate-rial,[13,38] exceeding the bulk modulus of γ-Si_3N_4 as well as the predicted values from DFT calculations. Its hardness and thermal stability, however, have not been investigated exper-imentally, 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 inves-tigations in terms of its elastic, physical, and optical proper-ties. More detailed information on the BM EoS fits and the elastic properties of sp-BeP_2N_4 is provided in the Supporting Information.
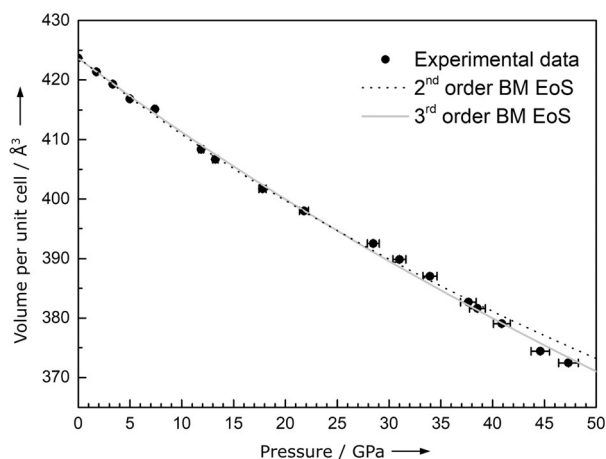

Figure 4. The pressure-volume data from pressure-dependent Rietveld refinements were fitted with a 2nd and 3rd order Birch-Murnaghan equation of state (BM EoS,), with fitting parameters provided in the main text. The isothermal bulk modulus of >300 GPa renders sp-BeP_2N_4 an ultraincompressible material.[13]

Recapitulating, phe-BeP$_2$N$_4$ 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$_2$N$_4$ was transformed into the spinel-type phase at 47 GPa and 1800 K using a laser-heated DAC. sp-BeP$_2$N$_4$ 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^{II}B$^V_2$N$_4$-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.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

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

How to cite: *Angew. Chem. Int. Ed.* **2020**, *59*, 2730–2734
Angew. Chem. **2020**, *132*, 2752–2756

[1] Q. Zhao, Z. Yan, C. Chen, J. Chen, *Chem. Rev.* **2017**, *117*, 10121, and references therein.

[2] W. Schnick, *Angew. Chem. Int. Ed.* **1999**, *38*, 3309; *Angew. Chem.* **1999**, *111*, 3511.

[3] A. Zerr, R. Riedel, G. Miehe, G. Serghiou, M. Schwarz, E. Kroke, H. Fueß, P. Kroll, R. Boehler, *Nature* **1999**, *400*, 340.

[4] M. Schwarz, G. Miehe, A. Zerr, E. Kroke, B. T. Poe, H. Fueß, R. Riedel, *Adv. Mater.* **2000**, *12*, 883.

[5] a) G. Serghiou, G. Miehe, O. Tschauner, A. Zerr, R. Boehler, *J. Chem. Phys.* **1999**, *111*, 4659; b) K. Leinenweber, M. O'Keeffe, M. Somayazulu, H. Hubert, P. F. McMillan, G. H. Wolf, *Chem. Eur. J.* **1999**, *5*, 3076.

[6] N. Scotti, W. Kockelmann, J. Senker, S. Traßel, H. Jacobs, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1435.

[7] T. Sekine, H. He, T. Kobayashi, M. Zhang, F. Xu, *Appl. Phys. Lett.* **2000**, *76*, 3706.

[8] N. Nishiyama, R. Ishikawa, H. Ohfuji, H. Marquardt, A. Kurnosov, T. Taniguchi, B.-N. Kim, H. Yoshida, A. Masuno, J. Bednarcik, et al., *Sci. Rep.* **2017**, *7*, 44755.

[9] N. Nishiyama, J. Langer, T. Sakai, Y. Kojima, A. Holzheid, N. A. Gaida, E. Kulik, N. Hirao, S. I. Kawaguchi, T. Irifune, et al., *J. Am. Ceram. Soc.* **2019**, *102*, 2195.

[10] A. Zerr, M. Kempf, M. Schwarz, E. Kroke, M. Göken, R. Riedel, *J. Am. Ceram. Soc.* **2002**, *85*, 86.

[11] J. Z. Jiang, F. Kragh, D. J. Frost, K. Ståhl, H. Lindelov, *J. Phys. Condens. Matter* **2001**, *13*, L515.

[12] I. Tanakaa, F. Oba, T. Sekine, E. Ito, A. Kubo, K. Tatsumi, H. Adachi, T. Yamamoto, *J. Mater. Res.* **2002**, *17*, 731.

[13] M. T. Yeung, R. Mohammadi, R. B. Kaner, *Annu. Rev. Mater. Res.* **2016**, *46*, 465.

[14] R. Marchand, F. Tessier, A. Le Sauze, N. Diot, *Int. J. Inorg. Mater.* **2001**, *3*, 1143.

[15] J. Haines, J. M. Léger, G. Bocquillon, *Annu. Rev. Mater. Res.* **2001**, *31*, 1.

[16] T. D. Boyko, A. Moewes, *J. Ceram. Soc. Jpn.* **2016**, *124*, 1063.

[17] W. Y. Ching, S.-D. Mo, I. Tanaka, M. Yoshiya, *Phys. Rev. B* **2001**, *63*, 64102.

[18] W. Y. Ching, S.-D. Mo, L. Ouyang, I. Tanaka, M. Yoshiya, *Phys. Rev. B* **2000**, *61*, 10609.

[19] J. Dong, J. Deslippe, O. F. Sankey, E. Soignard, P. F. McMillan, *Phys. Rev. B* **2003**, *67*, 340.

[20] E. Soignard, P. F. McMillan, K. Leinenweber, *Chem. Mater.* **2004**, *16*, 5344.

[21] F. J. Pucher, S. R. Römer, F. W. Karau, W. Schnick, *Chem. Eur. J.* **2010**, *16*, 7208.

[22] a) F. W. Karau, L. Seyfarth, O. Oeckler, J. Senker, K. Landskron, W. Schnick, *Chem. Eur. J.* **2007**, *13*, 6841; b) F. W. Karau, W. Schnick, *J. Solid State Chem.* **2005**, *178*, 135; c) F. J. Pucher, A. Marchuk, P. J. Schmidt, D. Wiechert, W. Schnick, *Chem. Eur. J.* **2015**, *21*, 6443; d) F. J. Pucher, F. W. Karau, J. Schmedt auf der Günne, W. Schnick, *Eur. J. Inorg. Chem.* **2016**, 1497.

[23] W. Y. Ching, S. Aryal, P. Rulis, W. Schnick, *Phys. Rev. B* **2011**, *83*, 155109.

[24] Y.-C. Ding, B. Xiao, *Acta Phys. Chim. Sin.* **2011**, *27*, 1621.

[25] M. Zhang, H. Yan, Y. Zhao, Q. Wei, *Comput. Mater. Sci.* **2014**, *83*, 457.

[26] W. L. Bragg, *Proc. R. Soc. London Ser. A* **1927**, *113*, 642.

[27] D. Hardie, K. H. Jack, *Nature* **1957**, *180*, 332.

[28] a) M. v. Stackelberg, R. Paulus, *Z. Phys. Chem. Abt. B* **1933**, *22*, 305; b) P. Eckerlin, A. Rabenau, *Z. Anorg. Allg. Chem.* **1960**, *304*, 218.

[29] S. Vogel, M. Bykov, E. Bykova, S. Wendl, S. D. Kloß, A. Pakhomova, S. Chariton, E. Koemets, N. Dubrovinskaia, L. Dubrovinsky, W. Schnick, *Angew. Chem. Int. Ed.* **2019**, *58*, 9060; *Angew. Chem.* **2019**, *131*, 9158.

[30] Within this contribution the spinel-type phase of BeP$_2$N$_4$ is denoted as sp-BeP$_2$N$_4$ rather than γ-BeP$_2$N$_4$, which has been used in some previous references to emphasize the structural relation to γ-Si$_3$N$_4$. A β-BeP$_2$N$_4$, however, has not been reported, as yet.

[31] a) C.-M. Sung, M. Sung, *Mater. Chem. Phys.* **1996**, *43*, 1; b) F. Gao, *Phys. Rev. B Condens. Matter Mater. Phys.* **2006**, *73*, 22.

[32] S. Horstmann, E. Irran, W. Schnick, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1873; *Angew. Chem.* **1997**, *109*, 1938.

[33] Crystal data of phe-BeP$_2$N$_4$ from single-crystal XRD refinement at ambient pressure: $M = 126.99$ g mol^{-1}, hexagonal, $R\bar{3}$ (no. 148), $a = 12.6979(15)$ and $c = 8.3595(10)$ Å, $V = 1167.3(5)$ Å^3, $Z = 18$, $\rho = 3.252$ g cm^{-3}, $\mu = 0.144$ cm^{-1}, synchrotron radiation ($\lambda = 0.28940$ Å, DESY, PETRAIII, P02.2), $T = 293$ K, 2852 observed reflections, 1241 independent reflections, 64 parameters, $R_{int} = 0.0656$, $R_\sigma = 0.0763$, $R1 = 0.0668$, $wR2 = 0.1403$, $GoF = 1.015$, residual electron density 1.145, -1.078 e Å^{-3}. CSD-1946333 contains the supplementary crystallographic data

for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[34] H. M. Rietveld, *J. Appl. Crystallogr.* **1969**, *2*, 65.

[35] Detailed information on the crystallographic data of sp-BeP$_2$N$_4$ from pressure-dependent Rietveld refinements is provided in the Supporting Information. CSD-1946347 (47.3 GPa), 1946344 (44.6 GPa), 1946343 (40.9 GPa), 1946342 (38.5 GPa), 1946340 (37.7 GPa), 1946339 (34.0 GPa), 1946338 (31.0 GPa), 1946337 (28.5 GPa), 1946336 (21.8 GPa), 1946335 (17.8 GPa), 1946334 (12.6 GPa), 1946346 (11.9 GPa), 1946349 (7.4 GPa), 1946341 (5.0 GPa), 1946348 (3.3 GPa), 1946332 (1.8 GPa), and 1946345 (1 atm) contain the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[36] R. Hoppe, S. Voigt, H. Glaum, J. Kissel, H. P. Müller, K. Bernet, *J. Less-Common Met.* **1989**, *156*, 105.

[37] a) F. D. Murnaghan, *Proc. Natl. Acad. Sci. USA* **1944**, *30*, 244; b) F. Birch, *Phys. Rev.* **1947**, *71*, 809.

[38] The ultraincompressible character, however, does not imply an intrinsic superhard behavior of sp-BeP$_2$N$_4$, as the hardness of a certain material correlates with its shear modulus rather than with its compressibility (bulk modulus).[13,15,16,25]