$Sr_3P_6O_6N_8$—a highly condensed layered phosphate†

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We describe the synthesis and the structure elucidation of $Sr_3P_6O_6N_8$, a novel, highly condensed layered phosphate.

During the last decades, inorganic phosphates have emerged from chemical commodities to advanced materials. Classical application areas of these basic inorganic compounds include usage as water softeners, fertilizers and coating materials.[1] Nowadays, phosphates are being used as ionic conductors,[2] catalysts in organic syntheses[3] and even as modern optical materials.[4–6] For example, KH_2PO_4 and $KTiOPO_4$ represent famous non-linear optical (NLO) materials used for frequency doubling (second harmonic generation, SHG), while ultraphosphates and phosphate glass (*e.g.* REP_4O_{11} and REP_5O_{14} where RE = lanthanide, and Nd^{3+}-doped vitreous phosphates) find applications as powerful laser materials.

The structural chemistry of inorganic phosphates has been widely studied in the past.[7] Classical representatives consist predominantly of orthophosphates, finite and infinite chain-phosphates, as well as ring-phosphates. Here Q^0 (non-linking) up to Q^2-type (double linking) PO_4-tetrahedra occur. Band-, layer- or framework-structures with Q^3 or even Q^4-type tetrahedra (comparable to silicates) have barely been identified. For higher condensed phosphates (exhibiting a degree of condensation (*i.e.* the molar ratio $P:O = \kappa > 1/3$)), only a few examples in the group of ultraphosphates have been described. Moreover, the maximum degree of condensation for oxophosphates is $\kappa = 0.40$.[8]

A further increase of cross-linking in phosphates, and thereby higher condensed structures, can be achieved in nitridophosphates or oxonitridophosphates by full or partial substitution O/N. With the integration of three-fold linking nitrogen, the structural diversity is significantly enhanced resulting in silicate-analogous networks, the latter being a consequence of the isolobal relation between P–N and Si–O which is further corroborated, for example, by HPN_2 (= PN(NH)) and PON that are isosteric to SiO_2. By variation of the molar ratio O:N, thus changing the framework charge, network structures with different topologies similar to silicate structures can be achieved. Complete substitution of O for N, yields nitridophosphates like MP_4N_7 with M = K, Rb, Cs[9] which adopt a network of corner-sharing PN_4-tetrahedra. The silicate analogy has further been demonstrated by the class of nitridosodalites[10] and related oxonitridosodalites.[11] However, complementing the diverse and rich structural chemistry of oxosilicates, new framework-types have been realized in (oxo-)nitridophosphates,[12] *e.g.* the first nitridic zeolite NPO.[13]

Recently, this novel framework-type containing large 12-ring channels was paralleled by its nitridosilicate analogue.[14] Another novel porous compound was obtained under high-pressure conditions—$P_4N_4(NH)_4(NH_3)$[15]—the first nitridic clathrate that traps ammonia molecules in an unique cage structure that had been previously predicted as a possible silica framework.[16,17] Highly condensed layer structures had not been realized so far; this includes oxophosphates and nitridophosphates, although the layered O′-form of $(P_2O_5)_x$ was discovered in the late 1940s.[18]

In this contribution we communicate the synthesis and structural characterization of a novel oxonitridophosphate, namely $Sr_3P_6O_6N_8$. Its P–O–N substructure exhibits a degree of condensation of $\kappa = 0.43$ thus representing the most condensed layer structure in phosphate chemistry so far.

A few known oxonitridophosphates (*e.g.* $M^I_3M^{III}P_3O_9N$ or $M^I_2M^{II}P_3O_9N$)[19,20] have been synthesized by conventional solid-state reactions.[21] By contrast, the preparation of $Sr_3P_6O_6N_8$ demands high-pressure conditions. Thereby, the so-called "azide approach", that is well established for the preparation of diverse nitridophosphates,[15,22,23] was transferred to the synthesis of oxonitridophosphates.‡ Employing a modified Walker module (multi-anvil assembly), $Sr_3P_6O_6N_8$ was obtained by heating a mixture of strontium azide $Sr(N_3)_2$ and phosphorus oxonitride PON at *ca.* 920 °C and 6 GPa (eqn (1)). Accordingly, the metal azide features a double role in the synthesis.

$$3Sr(N_3)_2 + 6PON \rightarrow \text{``}Sr_3N_2\text{''} + 8N_2 + 6PON \rightarrow$$
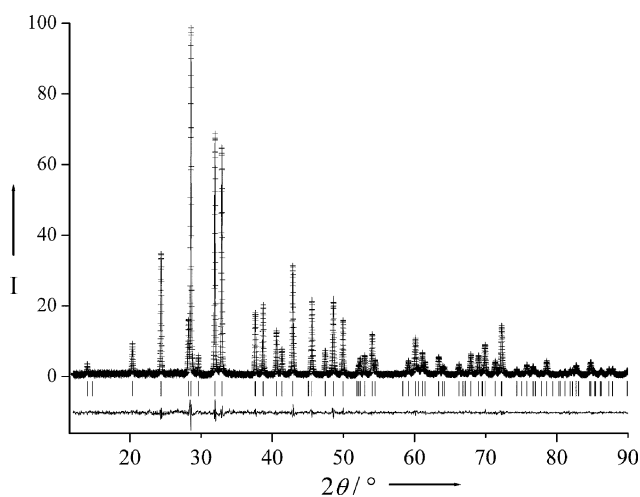$$Sr_3P_6O_6N_8 + 8N_2 \qquad (1)$$
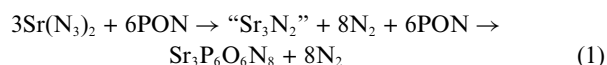
With the thermolysis of the azide in a closed system, a high N_2 partial pressure is generated and the dissociation of PON is suppressed at temperatures above 850 °C which are necessary for the crystallization of the product.[24] Simultaneously, the metal nitride that may be formulated as an intermediate (eqn (1)) is provided *in situ* for the reaction. Marginal amounts of amorphous, black phosphorus occurring during the synthesis of $Sr_3P_6O_6N_8$ coming from partial decomposition of the product can be removed by sublimation *in vacuo*. The elemental composition of the product was confirmed by energy dispersive X-ray analysis. All elements contained in the formula were detected and, within the accuracy of the measurements, the expected molar ratios were observed.

The crystal structure of $Sr_3P_6O_6N_8$ was solved on the basis of powder X-ray diffraction data by direct methods (EXPO;[25] and refined by the Rietveld method (GSAS;[26] Fig. 1).[27]

$Sr_3P_6O_6N_8$ exhibits an unprecedented phosphate layer resembling those of oxonitridosilicates (Fig. 2).[28] It is made up of Q^3-type PON_3-tetrahedra leading to a degree of condensation $\kappa = n(P):n(O,N) = 0.43$ for the $[P_6O_6N_8]^{6-}$ structure. According to $\{\textbf{\textit{uB}},3,1_{\infty^2}\}[(P_6^{[4]}O_6^{[1]}N_6^{[2]}N_{6/3}^{[3]})^{6-}]$,[29,30] the N atoms bridge two and three P atoms, respectively, whereas the O atoms are exclusively terminally bound to P. In contrast to nitridosilicates, $N^{[3]}$-connections

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† Electronic supplementary information (ESI) available: $^{31}P\{^1H\}$-C-REDOR curve of the ^{31}P resonance of $Sr_3P_6O_6N_8$. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b905136h

Fig. 1 Observed (crosses) and calculated (line) X-ray powder diffraction pattern (Cu Kα₁) as well as the difference profile of the Rietveld refinement of $Sr_3P_6O_6N_8$. Allowed peak positions are marked by vertical lines; background is subtracted.
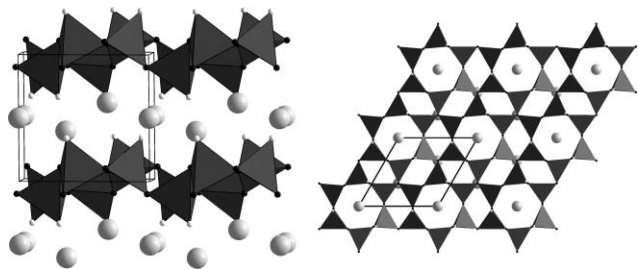
Fig. 2 Crystal structure of $Sr_3P_6O_6N_8$, left: view along [010], right: view perpendicular to one single layer along [001] (Sr^{2+} light gray, O^{2-} white, N^{3-} black).

are quite rare in nitridophosphate chemistry. The only examples yet known are P_3N_5,[31] HP_4N_7 (= P_4N_6NH),[32] P_4N_6O,[33] $Na_3P_6N_{11}$,[34] and $K_3P_6N_{11}$.[35]

Due to similar scattering factors, a direct experimental differentiation between O and N is impossible by X-ray methods. However, in the case of $Sr_3P_6O_6N_8$ complete O/N ordering is most probable as evidenced by ^{31}P solid-state NMR investigations, lattice energy calculations (MAPLE),[36] and P–O and P–N bond length differences. In the ^{31}P solid-state NMR spectrum of $Sr_3P_6O_6N_8$ (Fig. 3) a single resonance at $\delta_{iso} = 2.6$ ppm (principle components: −23, 2, 29 ppm) was observed agreeing with the single P site and its point group symmetry (1). According to ^{31}P chemical shift data of other P–O–N-compounds in the literature,[37–39] this resonance is indicative of a condensed PON_3-tetrahedra. The calculated partial MAPLE values (O^{2-}: 2526, N^{3-}: 6786–6410, Sr^{2+}: 1977–2111, P^{5+}: 14608 kJ mol⁻¹)[40] suggest that N atoms bridge the P atoms ($N^{[2]}$ and $N^{[3]}$ respectively) within the layer
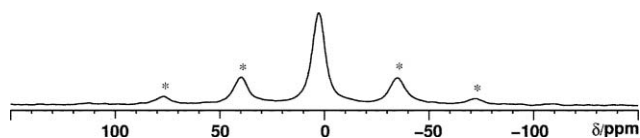
and the O atoms are bound terminally (Fig. 1). The MAPLE values vary in a range typical for these ions.[28,41] The presence of hydrogen atoms bound to the $N^{[2]}$ atoms has been excluded by solid-state NMR employing a $^{31}P\{^1H\}$ C-REDOR[42] experiment. Consequently, the bond length distribution in the N-bridges (158 and 164 pm) is according to P–$N^{[2]}$=P. The longest distance P–N (173 pm) was found at $N^{[3]}$. The shorter P–O bond lengths (153 pm) also corroborate the existence of exclusively PON_3-tetrahedra in $Sr_3P_6O_6N_8$. A similar O/N ordering was found in the layered oxonitridosilicates $M^{II}Si_6O_9N_4$[43] and $M^{II}Si_2O_2N_2$.[44]

The Sr^{2+}-ions along the channels (*cf*. Fig. 2) are coordinated distorted octahedrally by six O at a distance of 261 pm (Fig. 4, Sr2). In a longer distance (334 pm) these ions are further surrounded by six N atoms also in a distorted octahedral way. Around the second Sr site (Fig. 4, Sr1), six O (267–286 pm) and four N (281–322 pm) coordinate predominantly from different sides. The Sr–O and Sr–N distances range in the interval of the sum of their ionic radii.[45]
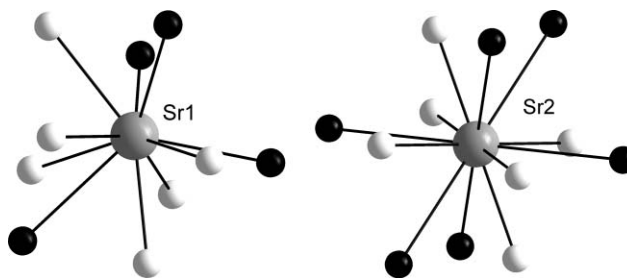
Fig. 4 Coordination of the Sr sites in $Sr_3P_6O_6N_8$ (Sr^{2+} gray, O^{2-} white, N^{3-} black).

The $[P_6O_6N_8]^{6-}$-layers in $Sr_3P_6O_6N_8$ are built up of condensed 6-rings and 4-rings (Fig. 2). These fundamental building units (FBUs) occur in other layered phosphates, but not simultaneously. In ultraphosphates (*e.g.* compositions like $M^{II}P_4O_{11}$ or $M^{III}P_5O_{14}$), besides small rings, there are always other rings with up to 16 tetrahedra resulting in large pore size layers.[8] Comparable layers can only be found within silicates,[29] whereas in purely oxidic silicates isostructural layers are prevented because oxygen usually avoids three-fold bridging positions. The oxonitridosilicates $M^{II}Si_6O_9N_4$[43] exhibit a related structure which, however, contain different 6-rings and additional 3-rings. However, an analogous structural motif can be identified in the structure of β-Si_3N_4.[46] There, isosteric Si_6N_{14}-layers are linked in the third dimension through SiN_4-tetrahedra (Fig. 5). A formal derivation of the structure of $Sr_3P_6O_6N_8$ from the β-Si_3N_4-structure can be
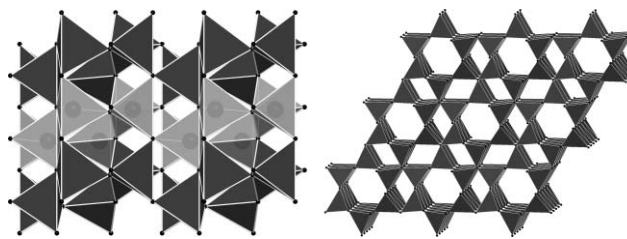
Fig. 5 Crystal structure of β-Si_3N_4, left: view along [010]. By removing every second layer (gray) and substituting the emerging terminal N by O atoms (besides a Si/P-replacement) results in topological similar layers as found in $Sr_3P_6O_6N_8$. Right: view along [001]. (Si^{4+} dark gray, N^{3-} black).

Fig. 3 ^{31}P MAS NMR spectrum of $Sr_3P_6O_6N_8$ at a spinning frequency of 3 kHz; spinning sidebands are marked with asterisks.

achieved by a separation of the Si_6N_{14}-layers and intercalating Sr^{2+}-ions, disregarding the atom assignment (P–Si, O–N). A compound that might be isostructural to $Sr_3P_6O_6N_8$, namely $Ba_3Si_6O_{12}N_2$, has been mentioned recently in a patent for a new green luminescent material for phosphor-converted white light (pc)LED applications. However a detailed crystallographic structure solution and refinement for the latter compound has not been communicated as yet.[47]

In conclusion, with $Sr_3P_6O_6N_8$ this class of phosphates gains a remarkable expansion of its structural chemistry. The highly condensed layered structure of $Sr_3P_6O_6N_8$, containing 6- and 4-rings of PON_3-tetrahedra, represents the first closed layer structure in phosphate chemistry. Layer structures with such a high degree of condensation were hitherto only known in silicate chemistry. The fact that the title compound is probably isostructural with a new green phosphor suggests an analogous application for $Sr_3P_6O_6N_8$. By doping it with lanthanides (e.g. Eu^{2+}) we are currently investigating the potential of $Sr_3P_6O_6N_8$ as a phosphor material. Consequently the substance class of the oxonitridophosphates could be developed to a new substance class for luminous applications. Prospectively, it would be interesting to access denser layer structures in oxonitridophosphates by a stepwise increase of the nitrogen ratio.

Acknowledgements

Notes and references

‡ Synthesis: $Sr_3P_6O_6N_8$ was synthesized from $Sr(N_3)_2$[48] and PON[49,50] by a high-pressure, high-temperature reaction in a Walker-type multi-anvil[51,52] assembly. In a glovebox (Unilab, MBraun, filled with dry Ar, $O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm) a finely ground mixture of the starting materials (approx. 50 mg) was placed into a capsule made of hexagonal boron nitride (Henze, Kempten) and compressed in a MgO-octahedron with an edge length of 18 mm (Ceramic Substrates, Isle of Wight). At 6 GPa the sample was heated over 15 min to about 920 °C, this temperature was maintained for 15 min, and finally the sample was cooled down to room temperature over 30 min. Further details concerning the assembly are described in the literature.[53] A crude product in the form of a black, cylindrical solid was isolated. To purify $Sr_3P_6O_6N_8$ from small amounts of black, amorphous phosphorus the product was pulverized and heated in vacuo at 680 °C for 5 d. $Sr_3P_6O_6N_8$ was obtained as a gray, air- and water stable, microcrystalline powder. Energy dispersive X-ray analysis measurements were performed on a JSM 6500F scanning electron microscope (Jeol; detector model 7418, Oxford Instruments). At 14 measuring points the ratios P : Sr = 2.5 (theoretical value according to the formula: 2.0) and N : O = 1.3 (theoretical value according to the formula: 1.3) were determined. These values are located within the accuracy of measurement for the method. $^{31}P\{^1H\}$ MAS NMR experiments were carried out on a BRUKER Avance II spectrometer equipped with a commercial 2.5 mm MAS NMR double-resonance probe at a magnetic field strength of 4.7 T. The chemical shift values refer to a deshielding scale and 85% H_3PO_4 used as an external reference. The C-REDOR experiment and the determination of the principle components were carried out as described in the literature.[54,55] Up to 1.2 ms on the unified dephasing scale, no dephasing was observed in the C-REDOR curves (see ESI†). Hence ^1H-^{31}P spin pairs at a distance smaller than approximately 1 pm can be ruled out at the noise level of the experiment. Together with half the maximum P–P distance in the unit cell, this proves the absence of H atoms in $Sr_3P_6O_6N_8$.

1 A. F. Holleman, E. Wiberg and N. Wiberg, Lehrbuch der Anorganischen Chemie, de Gruyter, Berlin, 102nd edn, 2007, pp. 798–799.
2 A. R. West, Basic Solid State Chemistry, John Wiley & Sons Ltd, Chichester, UK, 1999, pp. 336–341.
3 P. T. Nguyen, A. W. Sleight, N. Roberts and W. W. Warren, J. Solid State Chem., 1996, 122, 259–265.
4 C. N. R. Rao and J. Gopalakrishnan, New directions in solid state chemistry, Cambridge University Press, Cambridge, 1986.
5 J. D. Bierlein and H. Vanherzeele, J. Opt. Soc. Am. B, 1989, 6, 622–633.
6 M. J. Weber, J. Non-Cryst. Solids, 1990, 123, 208–222; R. K. Brow, J. Non-Cryst. Solids, 2000, 263–264, 1–28; J. H. Campbell and T. I. Suratwala, J. Non-Cryst. Solids, 2000, 263–264, 318–341.
7 A. Durif, Crystal Chemistry of Condensed Phosphates, Plenum Press, New York and London, 1995.
8 R. Glaum, Habilitationsschrift, Justus-Liebig-Universität Gießen, 1999.
9 K. Landskron, E. Irran and W. Schnick, Chem.–Eur. J., 1999, 5, 2548–2553.
10 W. Schnick and J. Lücke, Angew. Chem., 1992, 104, 208–209; W. Schnick and J. Lücke, Angew. Chem., Int. Ed. Engl., 1992, 31, 213–215; W. Schnick and J. Lücke, Z. Anorg. Allg. Chem., 1994, 620, 2014–2019; W. Schnick, N. Stock, J. Lücke, M. Volkmann and M. Jansen, Z. Anorg. Allg. Chem., 1995, 621, 987–992; F. Wester and W. Schnick, Z. Anorg. Allg. Chem., 1996, 622, 1281–1286.
11 N. Stock, E. Irran and W. Schnick, Chem.–Eur. J., 1998, 4, 1822–1828.
12 S. Correll, N. Stock, O. Oeckler and W. Schnick, Angew. Chem., 2003, 115, 3674–3677; S. Correll, N. Stock, O. Oeckler and W. Schnick, Angew. Chem., Int. Ed., 2003, 42, 3549–3552.
13 International Zeolite Association, Atlas of Zeolite Framework Types, http://www.iza-structure.org/databases/.
14 A. J. D. Barnes, T. J. Prior and M. G. Francesconi, Chem. Commun., 2007, 4638–4640.
15 F. Karau and W. Schnick, Angew. Chem., 2006, 118, 4617–4620; F. Karau and W. Schnick, Angew. Chem., Int. Ed., 2006, 45, 4505–4508.
16 M. D. Foster, O. D. Friedrichs, R. G. Bell, F. A. A. Paz and J. Klinowski, J. Am. Chem. Soc., 2004, 126, 9769–9775.
17 M. M. J. Treacy, K. H. Randall, S. Raho, J. A. Perry and D. J. Chadi, Z. Kristallogr., 1997, 212, 768–791.
18 C. H. MacGillavry, H. C. J. de Decker and L. M. Nijland, Nature, 1949, 164, 448–449.
19 W. Feldmann, Z. Chem., 1987, 27, 100–101.
20 R. Conanec, W. Feldmann, R. Marchand and Y. Laurent, Solid State Chem., 1996, 121, 418–422.
21 R. Marchand, W. Schnick and N. Stock, Adv. Inorg. Chem., 2000, 50, 193–233.
22 F. W. Karau and W. Schnick, J. Solid State Chem., 2005, 178, 135–141.
23 F. Karau and W. Schnick, Z. Anorg. Allg. Chem., 2006, 632, 231–237.
24 F. Tessier, A. Navrotsky, A. Le Sauze and R. Marchand, Chem. Mater., 2000, 12, 148–154.
25 A. Altomare, M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Rizzi, J. Appl. Crystallogr., 1999, 32, 339–340.
26 A. C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report LAUR, 2000, 86–748; B. H. Toby, J. Appl. Crystallogr., 2001, 34, 210–213.
27 Crystal data for $Sr_3P_6O_6N_8$ ($M_r = 656.8$ g mol^{-1}): trigonal, space group $P\bar{3}$ (no. 147), $a = 7.29667(5)$, $c = 6.02603(5)$ Å, $V = 277.851(5)$ Å^3, $Z = 1$; Stoe StadiP diffractometer (Debye–Scherrer geometry), Cu Kα_1 ($\lambda = 1.5406$ Å), $T = 298(2)$ K, step width of $2\theta = 0.1°$, $N_{obs} = 159$; 8 profile parameters (pseudo-Voigt), 17 atomic parameters, background function: shifted Chebyshev (20 coefficients), $R(F^2) = 0.0229$, w$R_p = 0.0263$, $R_p = 0.0202$; further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-419864†.
28 H. A. Höppe, PhD Thesis, Ludwig-Maximilians-Universität München, 2003; F. Stadler, PhD Thesis, Ludwig-Maximilians-Universität München, 2006.
29 F. Liebau, Structural Chemistry of Silicates, Springer, Berlin, 1985.
30 H.-J. Klein and F. Liebau, J. Solid State Chem., 2008, 181, 2412–2417.
31 W. Schnick, J. Lücke and F. Krumeich, Chem. Mater., 1996, 8, 281–286; S. Horstmann, E. Irran and W. Schnick, Angew. Chem., 1997, 109, 1938–1940; S. Horstmann, E. Irran and W. Schnick, Angew. Chem.,

Int. Ed. Engl., 1997, **36**, 1873–1875; S. Horstmann, E. Irran and W. Schnick, *Z. Anorg. Allg. Chem.*, 1998, **624**, 620–628.

32 S. Horstmann, E. Irran and W. Schnick, *Angew. Chem.*, 1997, **109**, 2085–2087; S. Horstmann, E. Irran and W. Schnick, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1992–1994; S. Horstmann, E. Irran and W. Schnick, *Z. Anorg. Allg. Chem.*, 1998, **624**, 221–227.

33 J. Ronis, B. Bondars, A. Vitola, T. Millers, J. Schneider and F. Frey, *J. Solid State Chem.*, 1995, **115**, 265–269.

34 A. Vitola, J. Ronis and T. Millers, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, 1990, **1**, 35–39.

35 H. Jacobs and R. Nymwegen, *Z. Anorg. Allg. Chem.*, 1997, **623**, 429–433.

36 R. Hoppe, *Angew. Chem.*, 1966, **78**, 52–63; R. Hoppe, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 95–106; R. Hoppe, *Angew. Chem.*, 1970, **82**, 7–16; R. Hoppe, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 25–34.

37 N. Stock, E. Irran and W. Schnick, *Chem.–Eur. J.*, 1998, **4**, 1822–1828.

38 A. Le Sauze, L. Montagne, G. Palavit and R. Marchand, *J. Non-Cryst. Solids*, 2001, **293–295**, 81–86.

39 S. Correll, N. Stock, O. Oeckler, J. Senker, T. Nilges and W. Schnick, *Z. Anorg. Allg. Chem.*, 2004, **630**, 2205–2217.

40 Lattice energy calculations were carried out with R. Hübenthal, *MAPLE, Programm zur Berechnung des Madelunganteils der Gitterenergie*, version 4, Universität Gießen, 1993.

41 K. Landskron, PhD Thesis, Ludwig-Maximilians-Universität München, 2001; K. Köllisch, PhD Thesis, Ludwig-Maximilians-Universität München, 2001.

42 J. C. C. Chan and H. Eckert, *J. Chem. Phys.*, 2001, **115**, 6095–6105.

43 F. Stadler and W. Schnick, *Z. Anorg. Allg. Chem.*, 2006, **632**, 949–954.

44 H. A. Höppe, F. Stadler, O. Oeckler and W. Schnick, *Angew. Chem.*, 2004, **116**, 5656–5659; H. A. Höppe, F. Stadler, O. Oeckler and W.

Schnick, *Angew. Chem., Int. Ed.*, 2004, **43**, 5540–5542; F. Stadler, O. Oeckler, H. A. Höppe, M. H. Möller, R. Pöttgen, B. D. Mosel, P. Schmidt, V. Duppel, A. Simon and W. Schnick, *Chem.–Eur. J.*, 2006, **12**, 6984–6990; O. Oeckler, F. Stadler, T. Rosenthal and W. Schnick, *Solid State Sci.*, 2007, **9**, 205–212; J. A. Kechele, O. Oeckler, F. Stadler and W. Schnick, *Solid State Sci.*, 2009, **11**, 537–543.

45 R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.*, 1969, **B25**, 925–946.

46 R. Grün, *Acta Crystallogr.*, 1979, **B35**, 800–804.

47 S. Shimooka, K. Uheda, M. Mikami, N. Kijima, H. Imura and K. Horibe, *Mitsubishi Chemical Corporation, PCT Int. Appl.*, WO088966, A1, 2007.

48 P. Remy-Genneté, *Ann. Chim.*, 1933, **19**, 263–352; P. Ehrlich and H. J. Seifert, in *Handbuch der Präparativen Anorganischen Chemie*, ed. G. Brauer, Ferdinand Enke Verlag, Stuttgart, 1987, vol. 2, p. 930.

49 L. Boukbir, R. Marchand, Y. Laurent, P. Bacher and G. Roult, *Ann. Chim. (Paris, Fr.)*, 1989, **14**, 475–481.

50 Amorphous PON was obtained by heating a mixture of one part $PO(NH_2)_3$ and three parts NH_4Cl in a ZrO_2-crucible in a continuous nitrogen flow at 680 °C for 48 h according to the equation $PO(NH_2)_3 + 3NH_4Cl \rightarrow PON + 3NH_4Cl + 2NH_3$. The mixture results from the reaction of $POCl_3$ with liquid NH_3 described by R. Klement and O. Koch, *Chem. Ber.*, 1954, **87**, 333–340.

51 D. Walker, M. A. Carpenter and C. M. Hitch, *Am. Mineral.*, 1990, **75**, 1020–1028.

52 D. Walker, *Am. Mineral.*, 1991, **76**, 1092–1100.

53 H. Huppertz, *Z. Kristallogr.*, 2004, **219**, 330–338.

54 M. Roming, C. Feldmann, Y. S. Avadhut and J. Schmedt auf der Günne, *Chem. Mater.*, 2008, **20**, 5787–5795.

55 J. Schmedt auf der Günne, *J. Magn. Reson.*, 2003, **165**, 18–32.