

PHOSPHORUS(V) NITRIDES: PREPARATION, PROPERTIES, AND POSSIBLE APPLICATIONS OF NEW SOLID STATE MATERIALS WITH STRUCTURAL ANALOGIES TO PHOSPHATES AND SILICATES.

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Abstract With the synthesis of pure, stoichiometric, and crystalline phosphorus nitride P_3N_5 an essential for the systematic investigation of higher phosphorus nitrides has become available. By solid state reaction of P_3N_5 with Li_3N and Ca_3N_2 , respectively, the following ternary compounds have been synthesized and have been characterized by their crystal structures and properties: Li_7PN_4 , $Li_{12}P_3N_9$, $Li_{10}P_4N_{10}$, $LiPN_2$, and Ca_2PN_3 . By defined heterogeneous ammonolyses of P_3N_5 the phosphorus nitride imides HPN_2 and HP_4N_7 have been obtained. Sodalite-type phosphorus nitrides (e.g. $M_{7-x}H_{2x}[P_{12}N_{24}]Z_{2-y}$; $M=Fe, Co, Ni, Mn$ etc.; $0 \leq x \leq 2$; $Z=Cl, Br$; $0 \leq y \leq 2$) are accessible via reaction of HPN_2 with metal chlorides MCl_2 . Silicon phosphorus nitride $SiPN_3$ is obtained by ammonolysis of $Cl_3SiNPCl_3$ followed by pyrolysis in an ammonia stream. All phosphorus nitrides obtained so far contain PN_4 -tetrahedra as characteristic building units which may be interconnected by common vertices showing differing degrees of condensation. Practical applications of phosphorus nitrides as solid state electrolytes and pigments are discussed.

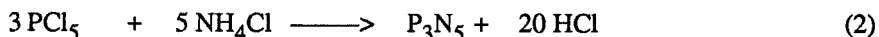
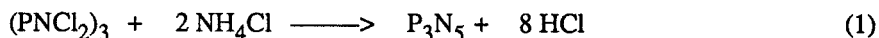
INTRODUCTION

In contrast to the huge number of well characterized molecular phosphorus-nitrogen-compounds (e.g. phosphazanes, phosphazenes) only fragmentary and contradictory results concerning syntheses, properties, and solid state structures of binary phosphorus(V) nitride as well as its ternary and higher compounds in combination with electro-positive elements have been elucidated so far. Starting from the successful synthesis of pure, defined, crystalline, and hydrogen-free P_3N_5 we began a large scale investigation on phosphorus nitrides.

PHOSPHORUS NITRIDE P_3N_5

Binary phosphorus nitride is accessible via reaction of PCl_5 or $(PNCl_2)_3$ with NH_4Cl according to Eq. (1) and (2). Because of the high amount of HCl formed this reaction

is performed using thick-walled quartz-ampoules [1].



According to SEM-, XRD-, ED-, HRTEM-, IR-, EXAFS-, ^{15}N - and ^{31}P -MAS-NMR-investigations phosphorus nitride is obtained as a colorless, microcrystalline solid. It is built up by a three-dimensional framework structure of corner-sharing PN_4 -tetrahedra. Two fifths of the nitrogen atoms each are covalently connected to three phosphorus atoms, the rest is bonded only to two P-atoms (average P-N-distance: 160 pm). As revealed by HRTEM and ED in the solid a stacking disorder along the crystallographic c-axis has been found.

ALKALI AND ALKALINE EARTH METAL PHOSPHORUS NITRIDES

Ternary phosphorus nitrides in combination with lithium or calcium are obtained by reaction of the respective metal nitrides and binary phosphorus nitride [2-6] in tungsten crucibles under pure nitrogen atmosphere. Crystallographic data and structural details concerning the P-N-partial structures of these compounds are summarized in Table I.

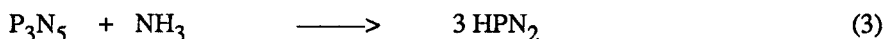
TABLE I Crystallographic data and structural details in Li- and Mg-P-N-phases.

Compound	Unit cell [pm, °]	Spcgrp.	No. of form. units	type of condensation of PN_4 -tetrahedra
Li_7PN_4	a=936.48(3)	P -4 3 n	8	isolated tetrahedra [2]
$\text{Li}_{12}\text{P}_3\text{N}_9$	a=1207.82(2) b=764.05(2) c=969.66(3) β =90.90(2)	C c	4	rings of 3 tetrahedra [3]
$\text{Li}_{10}\text{P}_4\text{N}_{10}$	a=1230.9(1)	F d -3 m	8	cage of 4 tetrahedra P_4O_{10} -analogously
LiPN_2	a=457.5(2)	I -4 2 d	4	β -cristobalite-type
Ca_2PN_3	a=518.92(1) b=1031.16(3) c=1128.45(3)	C m c a	8	infinite chains

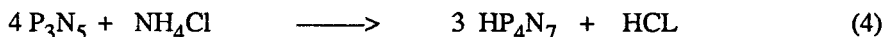
As revealed by impedance spectroscopy Li_7PN_4 and LiPN_2 are lithium ion conductors. Structural features of $\text{Li}_{12}\text{P}_3\text{N}_9$ and $\text{Li}_{10}\text{P}_4\text{N}_{10}$ also suggest a high lithium ion mobility in the solid.

PHOSPHORUS NITRIDE IMIDES

Phosphorus nitride imides HPN_2 [1] and HP_4N_7 [8] are obtained by heterogeneous ammonolyses of pure and crystalline P_3N_5 according to Eq. (3) and (4), respectively.



The reaction is carried out in a quartz ampoule and the ammonia used for this reaction *in situ* is produced by reaction of Mg_3N_2 with NH_4Cl [1].

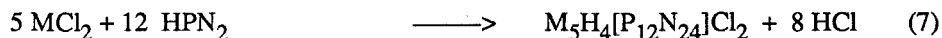
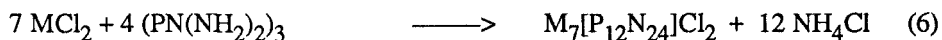
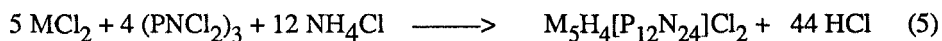


Both compounds (HPN_2 : $a=461.82(2)$, $c=702.04(3)$ pm, $I-4 2 d$, $Z=4$. HP_4N_7 : $a=480.33(8)$, $b=710.88(15)$, $c=1508.06(20)$ pm, $\beta=92.15(1)^\circ$, $Z=4$) are built up by three-dimensional framework structures of corner-sharing PN_4 -tetrahedra with the structure of HP_4N_7 being a shear-variant of the former one [8].

P-N-SODALITES

By using Zn_3N_2 instead of Mg_3N_2 for production of ammonia during ammonolysis of phosphorus nitride (cf. Eq. (3)) the new compound $\text{Zn}_5\text{H}_4[\text{P}_{12}\text{N}_{24}]\text{Cl}_2$ is formed [9]. By further reaction with ZnCl_2 it is transformed to a hydrogen-free compound $\text{Zn}_7[\text{P}_{12}\text{N}_{24}]\text{Cl}_2$ ($a=824.21(1)$ pm, $I-4 3 m$, $Z=1$). Both compounds are built up by three-dimensional framework-structures of corner-sharing PN_4 -tetrahedra. These arrangements are isoelectronic with and topologically equivalent to the well-known (Al/Si)-O-frameworks in normal sodalites [9]. On the basis of 8- and 12-membered rings of alternating P- and N- atoms typical β -cages are formed which are characteristic building units of zeolite-type structures.

Surprisingly P-N-sodalites are also accessible via more simple synthetic routes according to the Eq. (5), (6) and (7).



By these routes we succeeded to synthesize a considerable number of P-N-sodalites containing metal cations $M = \text{Co}, \text{Ni}, \text{Cr}, \text{Fe}, \text{Cu}, \text{Zn}, \text{Pb}$ and others. Even mixed P-N-sodalites containing two or more different metal cations are possible.

The most striking features of this new class of compounds are the strong color of some representatives (e.g. Fe, Co, Ni) as well as the remarkable chemical and thermal stability of these compounds (insoluble in common solvents, hot acids and bases; thermal stability up to approximately 800 °C).

SILICON PHOSPHORUS NITRIDE

Silicon phosphorus nitride SiPN_3 is synthesized by low-temperature ammonolysis of $\text{Cl}_3\text{Si-N=PCl}_3$ followed by pyrolysis at 900 °C in an ammonia atmosphere [10]. Silicon phosphorus nitride SiPN_3 ($a=904.12(6)$, $b=527.96(4)$, $c=470.21(4)$, $C\ m\ c\ 2_1$, $Z=4$) is isostructural with $\text{Si}_2\text{N}_2\text{NH}$ [11] and $\text{Si}_2\text{N}_2\text{O}$ [12]. Above 1000 °C thermal decomposition to $\alpha\text{-Si}_3\text{N}_4$ is observed [10].

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