

## 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.

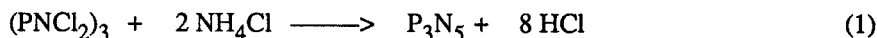
### INTRODUCTION

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-,  $^{15}\text{N}$ - and  $^{31}\text{P}$ -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  $\text{PN}_4$ -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.

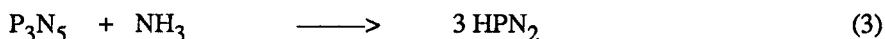
TABLE I Crystallographic data and structural details in Li- and Mg-P-N-phases.

Compound	Unit cell [pm, °]	Spcgrp.	No. of form. units	type of condensation of $\text{PN}_4$ -tetrahedra
$\text{Li}_7\text{PN}_4$	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) $\beta$ =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 $\text{P}_4\text{O}_{10}$ -analogously
$\text{LiPN}_2$	a=457.5(2)	I -4 2 d	4	$\beta$ -cristobalite-type
$\text{Ca}_2\text{PN}_3$	a=518.92(1) b=1031.16(3) c=1128.45(3)	C m c a	8	infinite chains

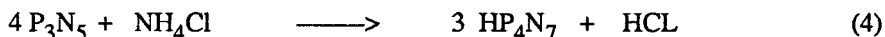
As revealed by impedance spectroscopy  $\text{Li}_7\text{PN}_4$  and  $\text{LiPN}_2$  are lithium ion conductors. Structural features of  $\text{Li}_{12}\text{P}_3\text{N}_9$  and  $\text{Li}_{10}\text{P}_4\text{N}_{10}$  also suggest a high lithium ion mobility in the solid.

### PHOSPHORUS NITRIDE IMIDES

Phosphorus nitride imides  $\text{HPN}_2$  [1] and  $\text{HP}_4\text{N}_7$  [8] are obtained by heterogeneous ammonolyses of pure and crystalline  $\text{P}_3\text{N}_5$  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  $\text{Mg}_3\text{N}_2$  with  $\text{NH}_4\text{Cl}$  [1].

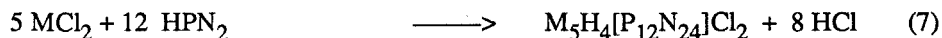
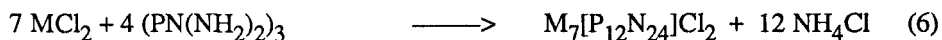
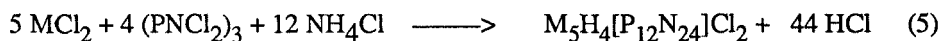


Both compounds ( $\text{HPN}_2$ :  $a=461.82(2)$ ,  $c=702.04(3)$  pm,  $I-4\ 2\ d$ ,  $Z=4$ .  $\text{HP}_4\text{N}_7$ :  $a=480.33(8)$ ,  $b=710.88(15)$ ,  $c=1508.06(20)$  pm,  $\beta=92.15(1)^\circ$ ,  $Z=4$ ) are built up by three-dimensional framework structures of corner-sharing  $\text{PN}_4$ -tetrahedra with the structure of  $\text{HP}_4\text{N}_7$  being a shear-variant of the former one [8].

### P-N-SODALITES

By using  $\text{Zn}_3\text{N}_2$  instead of  $\text{Mg}_3\text{N}_2$  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  $\text{ZnCl}_2$  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  $\text{PN}_4$ -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  $\beta$ -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  $\text{SiPN}_3$  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  $\text{SiPN}_3$  ( $a=904.12(6)$ ,  $b=527.96(4)$ ,  $c=470.21(4)$ ,  $C\ m\ c\ 2_1$ ,  $Z=4$ ) 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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