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CRYSTALLINE NITRIDOPHOSPHATES OBTAINED BY THERMAL REACTIONS

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Abstract Two types of crystalline nitridophosphates obtainable by simple thermal reactions are represented.

INTRODUCTION

Crystalline nitridophosphates are hitherto scarcely known. Marchand¹ obtained a crystalline sodium nitridophosphate the composition of which is assumed to be $\text{Na}_3\text{P}_3\text{O}_6\text{N}_2$ by heating of amorphous sodium polyphosphate under NH_3 flow at 550°C . This paper is concerned with two types of well-defined crystalline nitridophosphates found in our laboratory.

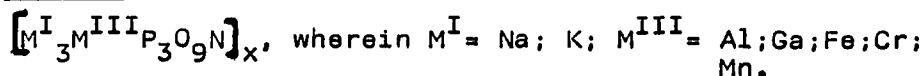
TWO TYPES OF CRYSTALLINE NITRIDOPHOSPHATES^{2,3,4}

These are:

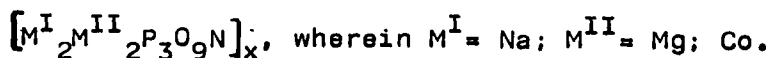
Type 1:



Type 2:



and



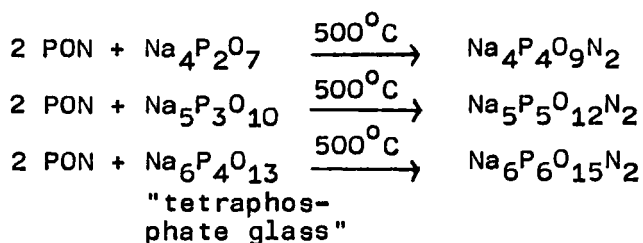
(Owing to simplicity the indices x are omitted subsequently)

The species of these two types are preparable by thermal reactions under relative simple conditions. The starting

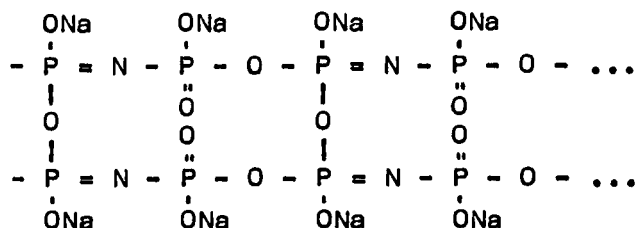
material, which must contain phosphorus with the oxidation number +5, nitrogen having the oxidation number -3, and the appropriate cation (Na or the cations M^I and M^{III} or M^I and M^{II}) and which may be a uniform compound

e.g. $Na_3P_3O_6(NH)_3 \cdot H_2O$ or a mixture of several compounds, including P-N-compounds as polymeric phosphorus oxide nitride PON, is heated for a period of about 1 hour at a temperature in the range of from 450 to 550 °C for preparing nitridophosphates of type 1 and in the range of from 550 to 850 °C for preparing the type 2 nitridophosphates. Since the sodium nitridophosphates are insoluble in water and the type 2 nitridophosphates are insoluble in dilute HCl it is easy to isolate pure samples by extraction of soluble by-products.

As to the nitridophosphates of type 1 typical reactions which allow to prepare defined species and which give some informations concerning the structure of the reaction products are represented:



Since the starting polymeric phosphorus oxide nitride is composed of $P=N-P-$ and $P-O-P$ groups⁵, it is believed that these structure elements remain in the reaction products for which a double chain constitution is supposed, e.g.



for $\text{Na}_4\text{P}_4\text{O}_9\text{N}_2$. This constitution is of the same kind as that of the silicate type amphiboles⁶. The number of cross-linking sites of the double chain results from the chain length of the used oligophosphate. In accordance with this structure conception all sodium nitridophosphates are isostructural (cf. Figure 1)

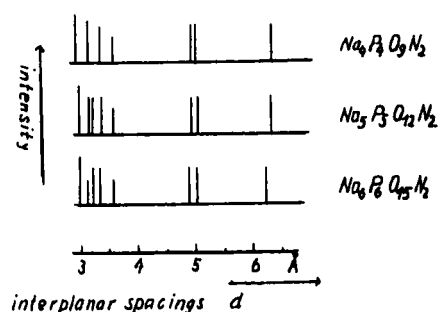
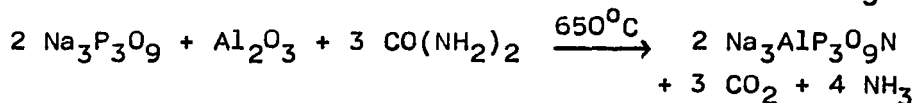
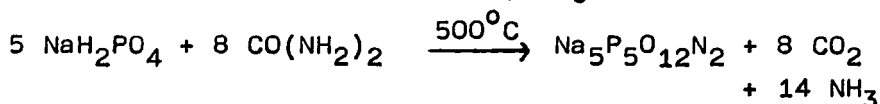
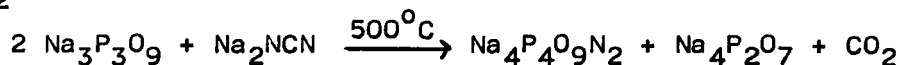


FIGURE 1. X-ray diffraction patterns of the nitridophosphates $\text{Na}_n\text{P}_n\text{O}_{3n-3}\text{N}_2$ ($n=4;5;6$).

Suitable agents ("nitridifying agents") for transforming phosphates and mixtures of phosphates and oxides into nitridophosphates are - besides PON - urea and other nitrogen derivatives of carbonic acid, e.g.



Another useful method for preparing nitridophosphates is the thermal decomposition of a condensed phosphate with Na_2NCN :

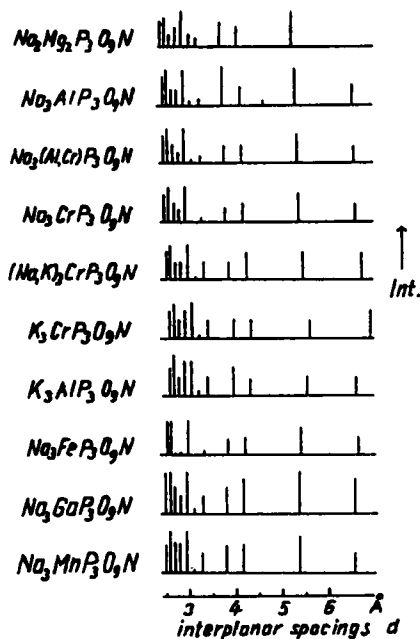


By heating this mixture at a temperature $< 450^\circ\text{C}$ Cyanamidophosphate is formed⁷.

All compounds of the type 2 nitridophosphates are iso-

structural, formation of mixed crystals was observed in the M^I sites, as well as in the M^{III} sites (cf. Figure 2)

FIGURE 2 X-ray
diffraction patterns
of $Na_2Mg_2P_3O_9N$ and
 $M^I_3M^{III}P_3O_9N$



Crystal structure analysis of type 1 and type 2 nitrido-phosphates could not yet made because we did not succeed in obtaining suitable single crystals.

The nitridophosphates of type 1 are insoluble in water, whereas the compounds of type 2 with M^{III} are insoluble even in boiling solutions of concentrated acid and alkali hydroxydes with the exception of boiling H_2SO_4 . Type 2 compounds with M^{II} are soluble in concentrated HCl .

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