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A NEW CLASS OF PHOSPHATE COMPOUNDS : INTRODUCTION OF NITROGEN IN THE TETRAHEDRAL PHOSPHORUS ENVIRONMENT

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Abstract Different possibilities to substitute nitrogen for oxygen in the PO₄ tetrahedron are illustrated.

INTRODUCTION

In this paper, we show that nitrogen can be introduced in the PO₄ tetrahedron as a substitute for oxygen. Nitrided phosphates are obtained, which are in a crystalline, an X-ray amorphous or a glassy form, depending on the case. They constitute a new class of phosphate materials. The substitution of nitrogen for oxygen is complete in ternary nitrides (PN₄ tetrahedra), partial in the PON phosphorus oxynitride (PO₂N₂ tetrahedra) and it can even be progressive in nitrided aluminophosphates or in phosphorus oxynitride glasses (PO_{4-x}N_x tetrahedra).

PN₄ TETRAHEDRA

PN₄ tetrahedra exist in ternary nitrides in which three structural types can be distinguished : wurtzite, cristobalite or anti-fluorite type.

The first type is illustrated by Mg₂PN₃ or Mn₂PN₃ compounds. Their normal tetrahedral structure is of wurtzite type. The parameters of the orthorhombic unit cell which results from the Mg(Mn)-P ordering are correlated to the parameters of the wurtzite hexagonal unit cell by the following relations :

$$a \cong 3 a_W \quad b \cong \sqrt{3} a_W \quad c \cong c_W$$

Magnesium (or manganese) and phosphorus atoms occupy half the tetrahedral sites of the hexagonal close-packing which is built up of nitrogen atoms.

The LiPN₂ nitride is an example of a "filled" cristobalite structure. Its structure consists of a skeleton of PN₄ tetrahedra which are linked to one another by their corners. This skeleton is analogous to the network of the SiO₄ tetrahedra in the high temperature β -cristobalite. The electroneutrality of this [PN₂]⁻ network is kept by the Li⁺ ions inserted in the

holes of the structure (Figure 1). The analogous sodium compound NaPN_2 crystallizes with the same structure.

In the lithium-phosphorus-nitrogen system, the Li_7PN_4 ternary nitride is also known. It crystallizes with an anti-fluorite type superstructure ($a = 2 a_0$). Lithium and phosphorus atoms are distributed in an ordered way on the tetrahedral sites of the cubic face-centered close-packing which is formed by the nitrogen atoms.

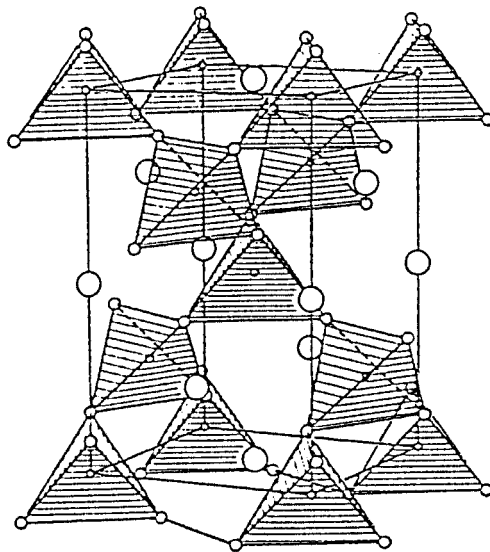
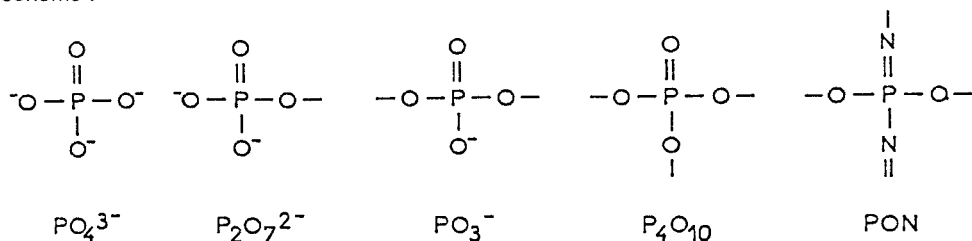


FIGURE 1 - Perspective view of the LiPN_2 structure.

PO_2N_2 TETRAHEDRA

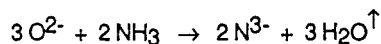
The crystalline PON oxynitride, isoelectronic with SiO_2 , has a β -cristobalite type structure. It thus comprises a tridimensional network of PO_2N_2 mixed tetrahedra. The analogy which exists between phosphorus oxynitride and silica is illustrated by the fact that under high pressure (45 kbars - 700°C) PON is transformed into the α -quartz type structure. It is interesting to notice that PON is the last member which completes the series : PO_4^{3-} monophosphate, $\text{P}_2\text{O}_7^{2-}$ diphosphate, PO_3^- polyphosphate, P_4O_{10} phosphoric anhydrid, in which the number of corners shared by the tetrahedra regularly goes from 0 to 4 as shown by the following scheme :



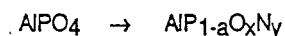
PO_{4-x}N_x TETRAHEDRA

Oxygen can be progressively replaced by nitrogen in the PO₄ tetrahedron. This has been shown by the determination of vitreous domains of nitrogen-containing phosphate glasses and by the obtention of amorphous nitrated aluminophosphates. The preparation of such phases can be performed through two general methods :

In the first method a purely oxygenated composition is nitrated under a reducing gaseous atmosphere. Ammonia presents the advantage of being both nitrating and reducing :



Thus, "AIPON" powders with high surface areas (>300 m².g⁻¹) are obtained from aluminum phosphate AlPO₄ (Figure 2), and M-P-O-N phosphorus oxynitride glasses (M = Li, Na, K) from the corresponding MPO₃ phosphates :



In the second method a solid reaction mixture containing a nitride-type compound is melted. PON phosphorus oxynitride can be advantageously used as a nitrogen source. Numerous vitreous compositions have been studied using this method, for example in the Na-M^{II}-P-O-N systems (M^{II} = Mn, Fe) (Figure 3).

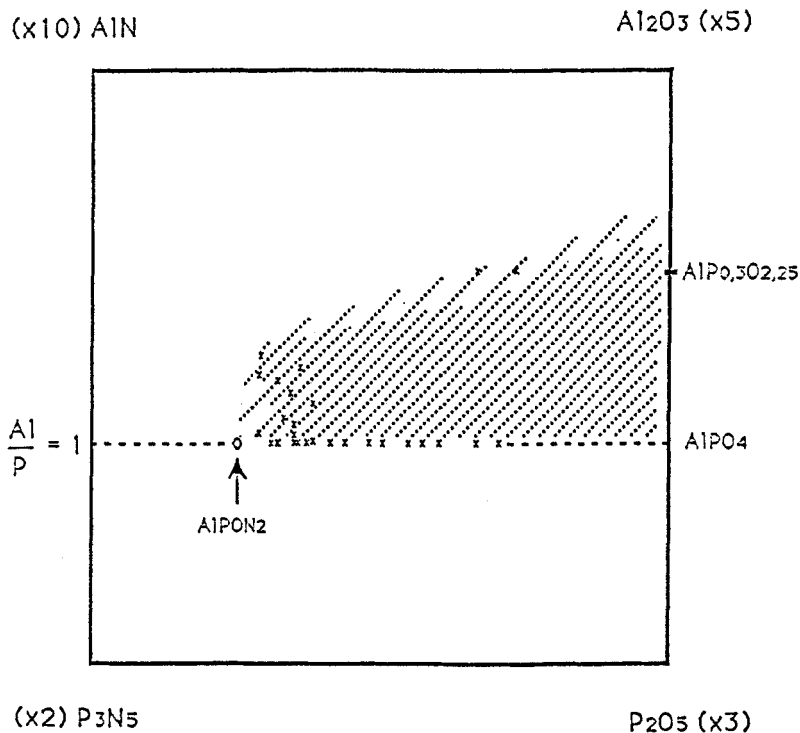


FIGURE 2 - "AIPON" oxynitride compositions in the AlN-Al₂O₃-P₂O₅-P₃N₅ square diagram.

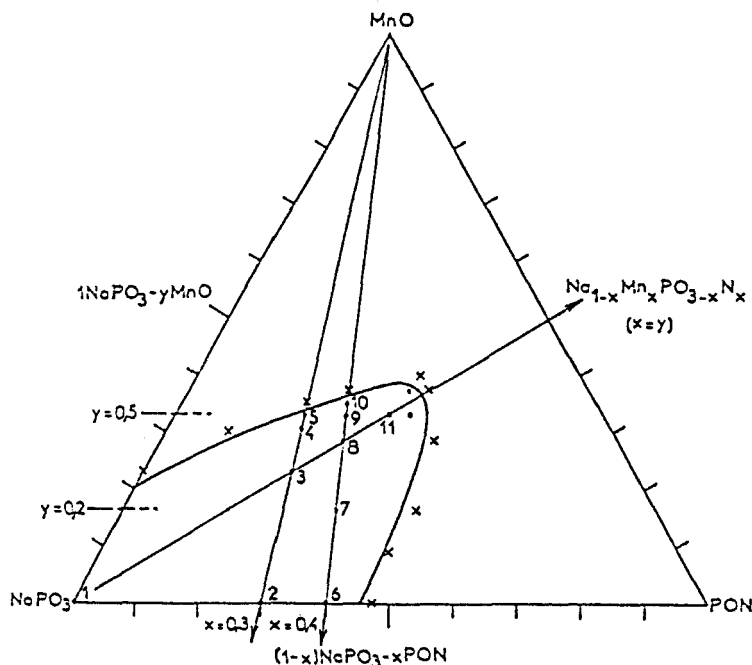


FIGURE 3 - Glass-forming region in the Na-Mn-P-O-N system.

The introduction of nitrogen in phosphate glasses leads to a considerable modification of their physical and chemical characteristics : increase in the glass transition and crystallization temperatures, viscosity, microhardness or chemical durability, decrease in the melting temperature and in the thermal expansion coefficient.

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