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FORMATION AND THERMAL DECOMPOSITION OF PHOSPHORUS OXYNITRIDE COMPOUNDS OF MAGNESIUM

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The formation of a previously unknown crystalline compound, Mg_3PN_3O, was found during studies on the reactions of phosphorus oxynitride and phosphorus pentoxide with magnesium nitride.

Earlier studies on the formation of compounds involving a mixed oxynitride coordination shell led to the formation of such salts for boron [1], aluminium [2], silicon [3–6] and germanium [7]. It was hypothesized that such compounds can also be obtained for phorphorus, an element in the neighbourhood of the above-mentioned ones in the periodic system.

A classification table is presented in Fig. 1, containing known monocentric (with a few exceptions) oxide, nitride and oxynitride phosphorus species. Hypothetical oxynitride species (in parentheses) are also given. The axes are described by the parameters $e_z(O^{2-})$ and $e_z(N^{3-})$, denoting the numbers of elementary negative charges formally introduced into the coordination shell by oxide and nitride ligands, respectively [3].

The anions PN_2O^{3-} and PN_3O^{6-} can be obtained through the reaction of phosphorus oxynitride with magnesium nitride and phosphorus nitride, or of magnesium salts (with PN_2^- or PN_3^{4-} anions) with magnesium oxide:

$$PNO + N^{3-} \rightarrow PN_2O^{3-}$$

$$PN_2^- + O^{2-} \rightarrow PN_2O^{3-}$$

It appears that magnesium oxide does not react with any nitride compounds of phosphorus below their decomposition temperatures, and hence the reactivity of phosphorus pentoxide with magnesium nitride was additionally studied.

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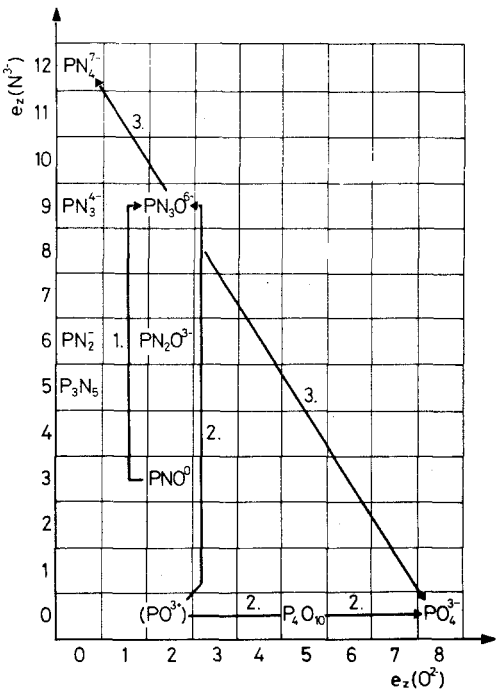

Fig. 1 Classification table of phosphorus oxynitride compounds

Experimental

Materials and apparatus

The following reactants were used in the studies:

PNO, prepared in our laboratory; P_2O_5, a product of Merck; and Mg_3N_2, prepared in our laboratory.

The reaction course was studied via thermal analysis methods on a derivatograph. The synthesis of the new compound and its thermal decomposition were carried out in a tube furnace under an inert atmosphere. After cooling, the reaction products were studied by means of X-ray and classical analysis.

Results

Thermoanalytical curves of the $PNO + Mg_3N_2$ mixture (1 : 1 mole ratio) are presented in Fig. 2. A weak exothermic effect is observed at 450°, and X-ray studies

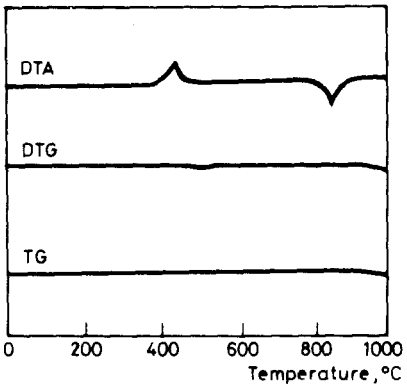

Fig. 2 TG, DTG and DTA curves of $PNO+Mg_3N_2$. $m=0.325$ g, N_2 atmosphere

Table 1 X-ray identification data for Mg_3PN_3O

d, Å	3.43	2.81	2.417	2.361	2.103	1.859	1.804	1.757	1.618	1.488
I/I_0	5	20	25	15	100	5	10	5	15	45

reveal the presence of a crystalline phase that is none of the known compounds in the Mg–P–N–O system. Its X-ray identification data are presented in Table 1.

Thermal curves of the $Mg_3N_2+P_2O_5$ mixture (3:2 mole ratio) are presented in Fig. 3. The process starts with a very strong exothermic effect at 320°. X-ray studies showed that the post-reaction mixture obtained at this temperature contains only amorphous products. The presence of crystalline $Mg_3(PO_4)_2$ was found in samples

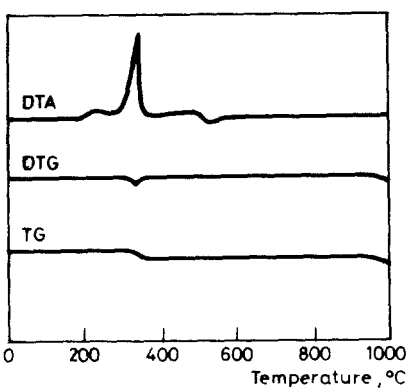

Fig. 3 TG, DTG and DTA curves of $P_2O_5+Mg_3N_2$. $m=0.071$ g, N_2 atmosphere

obtained at 550°. At 1100° the X-ray analysis additionally showed the presence of a new crystalline phase, identical with that obtained from the reaction of PNO with Mg_3N_2, where this phase had been obtained in a pure form without $Mg_3(PO_4)_2$. No substrates were found in either reaction after completion of the processes. Elemental analysis showed that the composition of the $PNO + Mg_3N_2$ post-reaction mixture corresponds to the stoichiometry Mg_3PN_3O.

Conclusions

It may be concluded from the results that an oxynitride salt, Mg_3PN_3O, is formed in the reaction of PNO and Mg_3N_2 (the transformation course is marked in the table in Fig. 1):

$$PNO + Mg_3N_2 \rightarrow Mg_3PN_3O$$

$$PNO + 2\,N^{3-} \rightarrow PN_3O^{6-}$$

The compound formed is a derivative of phosphoryl triamide $PO(NH_2)_3$.

The course of the reaction between P_2O_5 and Mg_3N_2 is more complicated. $Mg_3(PO_4)_2$ and Mg_3PN_3O are the identified products, probably formed as follows:

$$2\,P_2O_5 + 3\,Mg_3N_2 \rightarrow 2\,Mg_3PN_3O + Mg_3(PO_4)_2$$

$$(P_2O_5 \rightarrow PO^{3+} + PO_4^{3-})$$

$$(PO^{3+} + 3\,N^{3-} \rightarrow PN_3O^{6-})$$

$$P_2O_5 + 3\,N^{3-} \rightarrow PN_3O^{6-} + PO_4^{3-}$$

It is possible that, in the first stage, the reaction proceeds via an acidic-basic internal disproportionation of P_2O_5, which is shown schematically in the classification table in Fig. 1.

The thermal decomposition of Mg_3PN_3O takes place at 1250° and leads to magnesium orthooxyphosphate and probably magnesium azophosphate:

$$4\,PN_3O^{6-} \rightarrow 3\,PN_4^{7-} + PO_4^{3-}.$$

References

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Zusammenfassung — Bei der Untersuchung der Reaktion von Phosphoroxynitrid und Phosphorpentoxid mit Magnesiumnitrid wurde die Bildung der bis dahin unbekannten kristallinen Verbindung Mg_3PN_3O beobachtet.

Резюме — При изучении реакций оксинитрида фосфора и пятиокиси фосфора с нитридом магния было установлено образование ранее неизвестного кристаллического соединения Mg_3PN_3O.