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Topochemical transformations of hydrated sodium triphosphate, lithium triphosphate and mixed triphosphates

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Abstract

Topochemical transformations of crystalline $Na_5P_3O_{10} \cdot 6H_2O$, $Li_5P_3O_{10} \cdot 5H_2O$, and $NaLi_4P_3O_{10} \cdot 4H_2O$, amorphous $Na_2Li_3P_3O_{10} \cdot 4.3H_2O$ and mixed amorphous–crystalline $Na_{0.9}Li_{4.1}P_3O_{10} \cdot 4.4H_2O$ were studied by DTA, TG, DTG, IRS, XRD, and TLC methods in the temperature range 20–950°C. In all cases, except that of $Na_5P_3O_{10} \cdot 6H_2O$, the topochemical process proceeds through a degradation step with no subsequent formation of anhydrous triphosphate. The main crystalline product corresponds to the formula $Li_4P_2O_7$.

INTRODUCTION

Topochemical transformations of hydrated pentasodium triphosphate $Na_5P_3O_{10} \cdot 6H_2O$ occurring on heating that compound in air or in an atmosphere of inert gas consist of a number of consecutive processes, such as dehydration, first without then with degradation, resulting in the formation of mono- and diphosphate, recondensation of the latter to the low-temperature form of $Na_5P_3O_{10}$(**II**), its transformation to the high-temperature form of $Na_5P_3O_{10}$(**I**), which undergoes anionic rearrangement. Owing to the latter process, the molecular mass distribution of chain molecules in the solidified vitreous material corresponds to that theoretically predicted by van Wazer [1] and Galogaza et al. [2]. An exclusive feature of hydrated pentalithium triphosphate $Li_5P_3O_{10} \cdot 5H_2O$ is that its

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topochemical transformations proceed through an analogous scheme, but without the intermediate stage of recondensation of the mono- and diphosphate. Owing to this fact, it appears impossible to obtain anhydrous pentalithium triphosphate in either a direct or a dehydration scheme [3].

Hydrated sodium and lithium triphosphates form double salts with each other. An amorphous phase of variable composition $Na_yLi_{5-y}P_3O_{10} \cdot xH_2O$ (where $2 < y < 3$ and $x = 4.2$–4.5) has been separated from aqueous solutions of the system $Na_5P_3O_{10}$–$Li_5P_3O_{10}$–H_2O by means of an organic solvent [4]. That phase is co-precipitated with crystalline $Na_5P_3O_{10} \cdot 6H_2O$ at $y > 3$, and with $Li_5P_3O_{10} \cdot 5H_2O$ at $y < 2$. The crystalline double salt $NaLi_4P_3O_{10} \cdot 4H_2O$ separated from an aqueous solution of pentasodium triphosphate when lithium acetate was used as a precipitating agent.

In the present work we give the results of a comparative investigation of the topochemical transformations that take place on heating the crystal hydrates $Na_5P_3O_{10} \cdot 6H_2O$, $Li_5P_3O_{10} \cdot 5H_2O$, $NaLi_4P_3O_{10} \cdot 4H_2O$, the amorphous hydrous salt $Na_2Li_3P_3O_{10} \cdot 4.3H_2O$, and a sample of general composition $Na_{0.9}Li_{4.1}P_3O_{10} \cdot xH_2O$ (where $x = 4.4$); the last is a mixture of the amorphous salt $Na_2Li_3P_3O_{10} \cdot 4.3H_2O$ with a small amount of crystalline $Li_5P_3O_{10} \cdot 5H_2O$. The samples were heated in air at temperatures of 20–950°C.

EXPERIMENTAL

The materials used in the present study were chromatographically pure polycrystalline hexahydrate $Na_5P_3O_{10} \cdot 6H_2O$ (with mean crystal size d 0.06–0.6 mm) and finely crystalline pentahydrate $Li_5P_3O_{10} \cdot 5H_2O$ (d 0.02–0.07 mm) containing 0.3% P_1, 3.2% P_2, and 96.5% P_3 (P_1, P_2, and P_3 correspond to mono-, di-, and triphosphate phosphorus, respectively (in mass.%)). The tetrahydrate $NaLi_4P_3O_{10} \cdot 4H_2O$ in the form of fine white crystals (d 0.02–0.05 mm; 1.% P_2, 99.0% P_3) was precipitated at 20°C from saturated aqueous solutions of pentasodium triphosphate and lithium acetate with the proportion $Na_5P_3O_{10}$:CH_3COOLi 1:2. After mechanical initiation of the crystallization process the solution was kept for 22 days at 20°C; then the precipitate was separated, washed with ethanol, and dried for 2 days at a relative air humidity (RH) of 30–40%.

In order to obtain the amorphous salt $Na_2Li_3P_3O_{10} \cdot 4.4H_2O$ (1.1% P_1, 3.0% P_2, 95.9% P_3) and mixed amorphous-crystalline sample $Na_{0.9}Li_{4.1}P_3O_{10} \cdot 4.4H_2O$ (0.8% P_1, 2.5% P_2, 96.7% P_3) in the form of finely dispersed powders ($d \approx 0.001$ mm), aqueous solutions of $Na_5P_3O_{10}$ and $Li_5P_3O_{10}$ were mixed in the ratios of 2:3 and 1:4, respectively; an organic solvent (methanol or acetone) was added, and the viscous mass formed was separated from the solution and treated with fresh portions of organic solvent until it solidified. The solid obtained was dried in air at a RH of 30–40% for 2–3 days. The anionic composition of the samples was determined by quantitative thin-layer chromatography (TCL) with the use of a KTKh apparatus and thin layers of cellulose powder. The X-ray phase analyses were carried with a DRF-2.0 diffractometer (Cu Kα radiation), and a UR-20 spectrometer was used for the IR spectroscopy (IRS) studies (KBr disc method). Two types of derivatograph were used in the thermal analyses. An MOM OD-103 (with open quartz crucible) was applied in the study of all samples, and a 3434-C with microprocessor control (and open platinum crucible) was utilized in studying the crystal hydrates $Na_5P_3O_{10} \cdot 6H_2O$ and $Li_5P_3O_{10} \cdot 5H_2O$. The heating rate applied was 5–10 K min^{-1}.

RESULTS AND DISCUSSION

Despite the differences in mass of the samples studied ($m = 100$ instead of 4–18 mg) and differences in mean crystal size ($D = 0.06$–0.6 mm instead of 0.02–0.2 and 0.002–0.02 mm), the results of the derivatographic studies of $Na_5P_3O_{10} \cdot 6H_2O$ (Fig. 1) correspond, in general, to those obtained formerly in the studies by differential scanning calorimetry (DSC) [2]. The endothermic effect with peak temperature 141°C on the DTA curve corresponds to the overall elimination of crystallization water without discrimination of the component steps, including elimination of 2 mol H_2O without degradation, elimination of a further 3.0–3.5 mol H_2O with degradation and formation of a mixture of P_1 and P_2, and removal of the remaining 0.5–1.0 mol H_2O with recondensation of the mixture of P_1 and P_2 to form $Na_5P_3O_{10}$(**II**). The endothermic effect at 545°C corresponds to the transformation $Na_5P_3O_{10}(\mathbf{II}) \rightarrow Na_5P_3O_{10}(\mathbf{I})$, and that at 615°C results from melting of $Na_5P_3O_{10}$(**I**) with formation of chain phosphates of general formula $Na_{n+2}P_nO_{3n+1}$ where $1 < n \leqslant 14$. The observed slope on the DTA curve is due to a change in the physical state of the sample material, which climbed on the holder walls in the case of platinum, gold, and quartz holders and tended to accept a spherical form in a graphite holder [2].

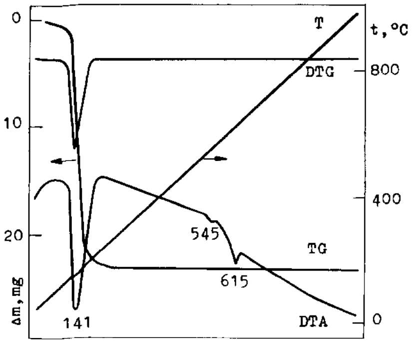

Fig. 1. The derivatogram of polycrystalline $Na_5P_3O_{10} \cdot 6H_2O$ ($d = 0.06$–0.6 mm; $m = 100$ mg; $\Delta m = 23.6$ mg; HR = 10 K min^{-1}; platinum pan).

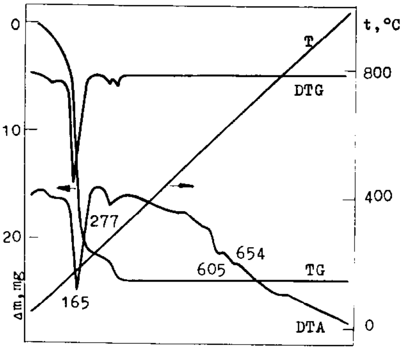

Fig. 2. The derivatogram of polycrystalline $Li_5P_3O_{10} \cdot 5H_2O$ ($d = 0.02$–0.07 mm; $m = 100$ mg, $\Delta m = 23.8$ mg; HR = 10 K min^{-1}; platinum pan).

Similar behaviour was also observed with the melt formed on heating $Li_5P_3O_{10} \cdot 5H_2O$ (Fig. 2). In this case the crystalization water was eliminated in two stages, which gave endothermic effects at 165 and 277°C. The first stage was an anionic dehydration which led to formation of an amorphous mixture of $P_1 + P_2$. In the second stage that mixture was transformed into the low-temperature form of anhydrous diphosphate $Li_4P_2O_7$(1) and high molecular-weight lithium phosphate of composition corresponding to $(LiPO_3)_n$ or $(LiPO_3)_n \cdot H_2O$. The second stage manifested itself by a leveling of the TG curve and a loss in mass of 23.8%. The endothermic effect at 654°C corresponds to melting of the $(LiPO_3)_n \cdot H_2O$, which proceeds at 656–665°C according to literature data [5–7]. The endothermic effect observed at 605°C may be regarded as a result of the superposition of the effect of melting of the eutectic system $Li_4P_2O_7(1) + (LiPO_3)_n \cdot H_2O$ (the temperature range of which is considered to be 603–608°C [6, 7]) and the endothermic effect of a phase transition of the low-temperature form of tetralithium diphosphate into the high-temperature form $(Li_4P_2O_7)$(h) which takes place at 615°C. The two effects were recorded separately by means of DSC [3]: the melting of the eutectics $Li_4P_2O_7(1) + (LiPO_3)_n \cdot H_2O$ at 609°C and the transition $Li_4P_2O_7(1) \rightarrow Li_4P_2O_7$(h) at 615°C.

It follows from Fig. 3, that at the stage of the elimination of crystalization water (endothermic effects at 130 and 140°C), which ends at 200–220°C, the tetrahydrate of the double salt $NaLi_4P_3O_{10} \cdot 4H_2O$ is reminiscent of $Na_5P_3O_{10} \cdot 6H_2O$ rather than $Li_5P_3O_{10} \cdot 5H_2O$. It does not mean, however, that the tetrahydrate (like $Na_5P_3O_{10} \cdot 6H_2O$) is transformed into the corresponding double salt in either a direct or a dehydration scheme. According to the data of quantitative TLC analysis (Table 1), at 130 and 140°C the sample contains 91.5% P_3 and 81.9% P_3, respectively, and at 200°C the content of P_3 is reduced to 9.8%; on further heating to 700°C the limits 1.8–3.7% P_3 are transgressed. It is seen, therefore, that as in the case of $Li_5P_3O_{10} \cdot 5PH_2O$, it is impossible to obtain an anhydrous salt of the type

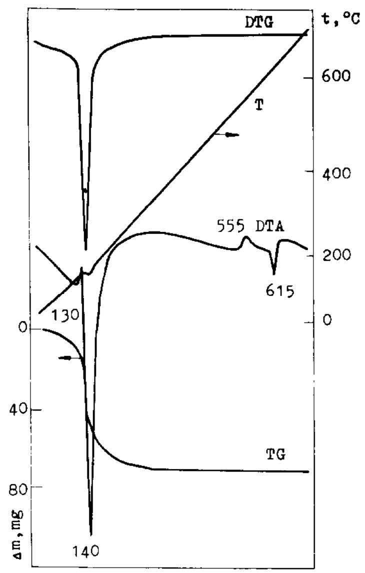

Fig. 3. The derivatogram of fine-crystalline $NaLi_4P_3O_{10} \cdot 4H_2O$ ($d = 0.02–0.05$ mm; $m = 400$ mg; $\Delta m = 72.0$ mg; HR = 5 K min^{-1}; quartz pan).

$NaLi_4P_3O_{10}$ by thermal treatment of $NaLi_4P_3O_{10} \cdot 4H_2O$ under the present conditions.

The values of $P_4 + P_5 + P_{start}$ given in Table 1 represent the overall contents of phosphorus in the form of tetraphosphate, pentaphosphate, and the phosphates retained in the start spot of the chromatogram. A feature of the TLC analysis of the products of the thermal decomposition of $NaLi_4P_3O_{10} \cdot 4H_2O$ is that, starting with temperatures of 200–220°C, continuous zones, accounting for the formation of phosphates with $n > 5$

TABLE 1

The results of quantiative TLC analysis of the products of the thermal decomposition of $NaLi_4P_3O_{10} \cdot 4H_2O$ [a]

t (°C)	Δm (°C)	P_1 [b]	P_2 [b]	P_3 [b]	$P_4 + P_5 + P_{start}$ [b]
20	0	0	1.0	99.0	0
130	3.6	3.1	5.4	91.5	0
140	12.5	5.8	12.3	81.9	0
200	16.2	4.5	72.1	9.8	13.6
300	17.8	1.7	62.6	2.3	33.4
400	17.9	2.7	52.3	1.8	43.2
530	18.0	1.9	58.7	2.8	36.6
555	18.0	2.6	57.8	2.0	37.6
615	18.0	1.8	58.6	2.6	37.0
700	18.0	3.2	56.7	3.7	36.4

[a] HR = 5 K min^{-1}. [b] Phosphorus content (mass.%).

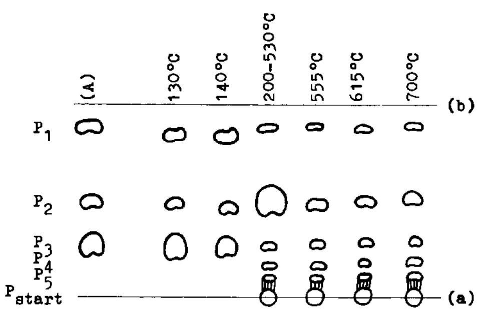

Fig. 4. TLC results of the products of the thermal decomposition of $NaLi_4P_3O_{10} \cdot 4H_2O$ (HR = 5 K min^{-1}; (A), standard mixture of P_1, P_2 and P_3; (a), start line; (b), front line).

(Fig. 4), appear between the P_5 and P_{start} spots. Besides, insoluble products appear in the reaction mixture. To transform those products into an aqueous solution it was necessary to treat the mixture with the disodium salt of ethylenediaminetetraacetic acid (EDTA) or with an aqueous suspension of the KU-2 cation exchange resin in the NH_4^+ form.

No formation of cyclic phosphates was found by two-dimensional TLC in the products of the thermal transformation of $NaLi_4P_3O_{10} \cdot 4H_2O$ or in the products of the thermal treatment of $Li_5P_3O_{10} \cdot 5H_2O$. In this light, in the presentation of the composition of the high molecular weight products, priority is given to the chain compounds $(LiPO_3)_n \cdot H_2O$ rather than to the cyclic compounds $(LiPO_3)_n$. No absorption bands characteristic of cyclic phosphates were found in the IR spectra (Fig. 5). It means, that cyclic phosphates are absent in the products of thermal treatment, both before and after their solubilization. With increasing heating temperature the intensity of the IR absorption bands at 1645 and 1660 cm^{-1}, resulting from deformation vibrations of water molecules $\delta(H_2O)$, decreases and finally disappears. At the same time one may observe the appearance and increase in intensity of absorption zones at 715 cm^{-1} (ν_s(POP)) and 1200 cm^{-1} ($\nu_{as}(PO_3)$) characteristic of diphosphates, and a band at 1275 cm^{-1} (ν_{as}(OPO)) characteristic of high molecular weight phosphates.

The order of the formation of new crystal phases on heating $NaLi_4P_3O_{10} \cdot 4H_2O$ is shown in Fig. 6. The original phase disappears at 200–220°C. In this temperature region appear and increase in intensity the diffraction peaks of diphosphate $Li_4P_2O_7$(1), which remains the only crystalline product of topochemical transformations of $NaLi_4P_3O_{10} \cdot 4H_2O$ up to 530°C. A new non-identified phase appears in the zone of endothermic effect at 555°C (see Fig. 4). The diffraction peaks increase in intensity if the sample is melted (endothermic effect at 615°C; Fig. 4), then cooled. The existence of that phase, which may be a high molecular weight double phosphate $[(Na,Li)PO_3]_n \cdot H_2O$, was noted earlier [4]. On comparing the activity of crystalline and amorphous hydrated salts of identical or similar composition, it was shown that the rate of the initial stages of

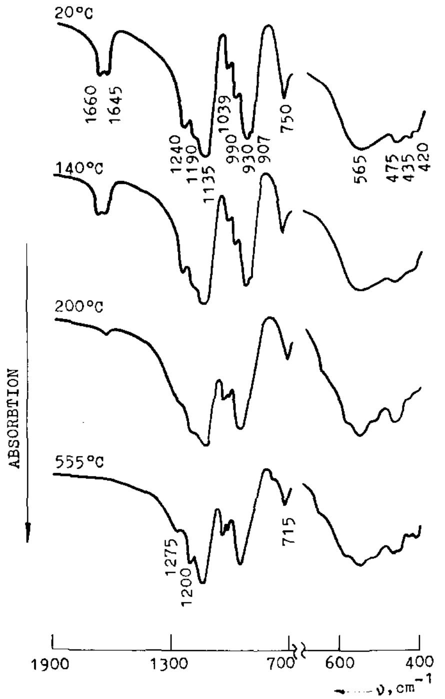

Fig. 5. IR spectra of fine-crystalline $NaLi_4P_3O_{10} \cdot 4H_2O$ and of the products of thermal decomposition of $NaLi_4P_3O_{10} \cdot 4H_2O$ (HR = 5 K min^{-1}).

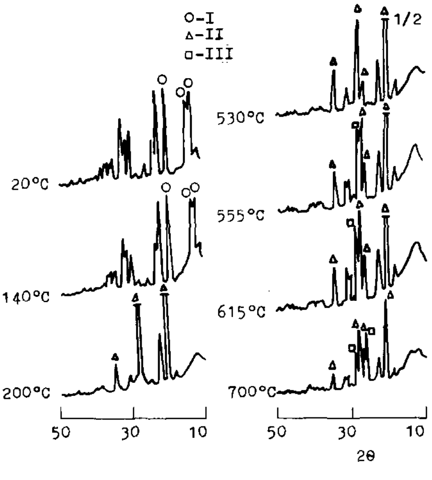

Fig. 6. X-ray pattern of fine-crystalline $NaLi_4P_3O_{10} \cdot 4H_2O$ and of the products of its thermal decomposition (HR = 5 K min^{-1}; **I**, $NaLi_4P_3O_{10} \cdot 4H_2O$, **II**, $Li_4P_2O_7(1)$; **III**, unidentified phase).

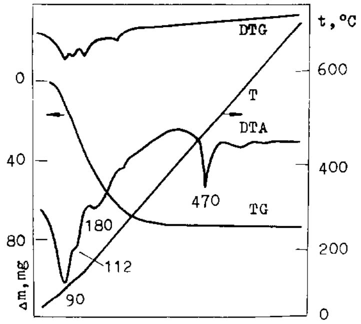

Fig. 7. The derivatogram of amorphous $Na_2Li_3P_3O_{10} \cdot 4.3H_2O$ ($d \approx 0.001$ mm; $m = 400$ mg; $\Delta m = 73.0$ mg; HR = 5 K min^{-1}; quartz pan).

topochemical and mechanochemical transformations of amorphous materials is higher than that of crystalline samples, whereas for later stages this order may be reversed [8, 9]. Thus, on transition from crystalline $NH_4Mg_2P_3O_{10} \cdot 6H_2O$ to amorphous $NH_4Mg_2P_3O_{10} \cdot 7H_2O$ the endothermic effect of dehydration is shifted by 70°C toward lower temperatures, whereas the exothermic effect of crystalization of the end product is shifted 160°C toward higher temperatures.

In our case, in analogous transitions the effects of the initial and final stages were both shifted in the same direction toward lower temperatures. Elimination of hydration water from the amorphous $Na_2Li_3P_3O_{10} \cdot 4.3H_2O$ with simultaneous anionic rearrangement gives endothermic effects at 90, 112, and 180°C, and the effect corresponding to melting of the solid residue appears at 470°C (Fig. 7). In the case of the mixed amorphous-crystalline sample of overall composition $Na_{0.9}Li_{4.1}P_3O_{10} \cdot 4.4H_2O$, the above processes give three endothermic effects at 90, 140, and 182°C, and one endothermic effect at 595°C (Fig. 8).

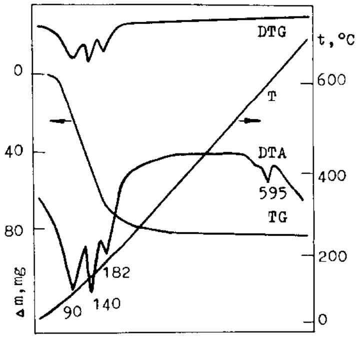

Fig. 8. The derivatogram of the mixed amorphous-crystalline sample of overall composition $Na_{0.9}Li_{4.1}P_3O_{10} \cdot 4.4H_2O$ ($d \approx 0.001$ mm; $m = 400$ mg; $\Delta m = 84.0$ mg; HR = 5 K min^{-1}; quartz pan).

TABLE 2

The results of XRD and TLC analyses of the products of the thermal decomposition of amorphous and mixed amorphous–crystalline samples [a]

Sample	t (°C)	Δm (%)	P_1 [b]	P_2 [b]	P_3 [b]	$P_4 + P_5 + P_{start}$ [b]	Crystalline phases [c]
$Na_2Li_3P_3O_{10} \cdot 4.3H_2O$ (amorphous)	400	18.3	0	68.4	0	31.6	**II**, **III**
$Na_{0.9}Li_{4.1}P_3O_{10} \cdot 4.4H_2O$ (mixed amorphous–crystalline)	400	21.0	0	60.0	0	40.0	**II**, **III**

[a] HR = 5 K min^{-1}. [b] Phosphorus content (mass.%). [c] **II**, $Li_4P_2O_7$(1); **III**, unidentified phase.

Amorphous and mixed amorphous–crystalline forms are characteristic the relatively low crystallization temperature of the above-mentioned unidentified phase, which appears in the reaction mixture at 400°C (Table 2). Besides, there is almost no P_1 and P_3 in the reaction mixture, the essential components of which are a diphosphate and a polyphosphate of high molecular weight. A unique feature of the topochemical transformations of crystalline $NaLi_4P_3O_{10} \cdot 4H_2O$, amorphous $Na_2Li_3P_3O_{10} \cdot 4.3H_2O$, and mixed amorphous–crystalline $Na_{0.9}Li_{4.1}P_3O_{10} \cdot 4.4H_2O$ was that the stage of anionic dehydration was not followed by the stage of recondensation and formation of anhydrous triphosphate observed in the case of $Na_5P_3O_{10} \cdot 6H_2O$. This result correlates well with the data previously obtained in studies of the thermal transformations of $Li_5P_3O_{10} \cdot 5H_2O$ [3], amorphous salts $Na_yLi_{5-y}P_3O_{10} \cdot xH_2O$ ($2 < y < 3$, $x = 4.2$–4.5) [4], and mixtures of $LiH_2PO_4 + 2Li_2HPO_4$ and $LiH_2PO_4 + Li_4P_2O_7$(1) [10].

It is generally known [1] that the amorphous phase plays an important role in the recondensation processes that occur in obtaining pentasodium triphosphate from mixtures of the type $P_1 + P_2$. In our case only monophosphate was in the amorphous state, because the diphosphate is easily crystallized, thus losing its activity and taking no part in further transformations. It is important to state that in our case the processes resulting in formation of stable $Li_4P_2O_7$(1) are of great importance. This accounts for the high content of diphosphate in the products. In our conditions that contents reached 72% P_2 (see Table 1), and in some cases, as in heating the mixtures of $LiH_2PO_4 + 2Li_2HPO_4$ in a stream of water vapour, it reached 95–97% P_2 [10].

This may be accounted for by the fact that stable $Li_4P_2O_7$(1) hardly reacts with amorphous monophosphate, but more with crystalline $(LiPO_3)_n \cdot H_2O$ or $[(Na,Li)PO_3]_n \cdot H_2O$ to form anhydrous triphosphate. Such a reaction is effected in the melt, but when this is cooled the prevailing process is the crystallization of $Li_4P_2O_7$(1) and of a polyphosphate of high molecular weight. As a result, the vitreous product obtained contains little P_3 but much P_2 and $P_4 + P_5 + P_{start}$. Thus the vitreous material obtained on heating

$NaLi_4P_3O_{10} \cdot 4H_2O$ at 700°C with subsequent cooling of the melt formed (see Table 1) contains 56.7% P_2, 36.4% $P_4 + P_5 + P_{start}$, and only 3.7% P_3.

REFERENCES

1 J.R. Van Wazer, Phosphorus and its Compounds, Vol. 1, Interscience, New York, 1958.
2 V.M. Galogaza, E.A. Prodan, V.A. Sotnikova-Yuzhik, D.U. Skala, N.V. Bulavkina and S.I. Pytlev, Thermochim. Acta, 106 (1986) 141.
3 V.M. Galogaza, E.A. Prodan, G.V. Peslyak, V.A. Sotnikova-Yuzhik and S.A. Prodan, J. Therm. Anal., 34 (1988) 11.
4 V.A. Sotnikova-Yuzhik, E.A. Prodan and G.V. Peslyak, Zh. Neorg. Khim., 34 (1989) 1166 (in Russian).
5 T.Y. Ten and F.A. Hummel, J. Am. Ceram. Soc., 44 (1961) 206.
6 M.M. Markovits, R.T. Harris and W.N. Hawley, J. Inorg. Nucl. Chem., 22 (1961) 293.
7 R.K. Osterheld, J. Inorg. Nucl. Chem., 30 (1968) 3173.
8 E.A. Prodan, React. Solids, 8 (1990) 299.
9 E.A. Prodan, Sib. J. Chem., 5 (1991) 123.
10 V.M. Galogaza, E.A. Prodan, V.A. Sotnikova-Yuzhik, G.V. Peslyak and L. Obradovic, J. Therm. Anal., 31 (1986) 897.