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A STUDY OF THE THERMAL PREPARATION AND STABILITY OF c-$Zn_2P_4O_{12}$

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ABSTRACT

The thermal preparation of zinc cyclo-tetraphosphate c-$Zn_2P_4O_{12}$ starting from $Zn(H_2PO_4)_2 \cdot 2H_2O$ has been investigated using thermal analysis (TA) techniques: namely, dynamic TA and TA under quasi-isothermal quasi-isobaric conditions. Moreover, calcinates from the starting phosphate and from the intermediates $Zn(H_2PO_4)_2$ and $ZnH_2P_2O_7$ have been prepared under isothermal–isobaric conditions in an electric furnace, and analysed. In this way, the temperature regions within which the intermediates and the product exist, and the kinetics of their formation were determined. The course of the reaction and reaction temperatures, rates and yields are markedly influenced by the water vapour pressure in the calcinate area. The thermal stability of c-$Zn_2P_4O_{12}$, its modification transformation, and the incongruent melting and partial recrystallization of the melting products have been confirmed by high-temperature DTA under various atmospheric conditions, by thermogravimetry, by the DTA/DSC method, and by determination of density as a function of the calcination temperature.

INTRODUCTION

The method of preparation of c-$Zn_2P_4O_{12}$ used in our work is based on thermal dehydration of $Zn(H_2PO_4)_2 \cdot 2H_2O$ [1–4]. The literature gives results of dynamic thermal analysis (TA) investigations of this dehydration process [1–3], but these and other data [4] do not provide a sufficient basis for the synthesis of c-$Zn_2P_4O_{12}$ on an industrial scale. The product possesses several very useful properties [5], so it has many applications. In particular, we have evaluated its applications as a special inorganic thermostable material [6,7], and a balastless microelement fertilizer with long-term action [8]. We have also found it to possess distinct anti-corrosion and corrosion-inhibition properties [9]. The properties of the product are further improved if it is prepared with various admixtures, particularly those of alkali earths [10,11]. Preparation of such products necessitates [12,13] determination and control of the conditions of the condensation reaction producing pure c-$Zn_2P_4O_{12}$.

In previous communications [14–17], we have considered the thermal preparation of cyclo-tetraphosphates of other divalent metals, starting from described TA methods [18]. It has been established that the courses, temperatures, kinetics and yields of the dehydration and condensation reactions are markedly affected by the water vapour pressure in the calcinate area. These observations have also been applied in an investigation of the reaction of formation of c-$Zn_2P_4O_{12}$ [19]. With regard to the important application potential of this product, its synthesis has been submitted to a more detailed examination in the present work.

Thermal stability is essential for some applications of cyclo-tetraphosphates of divalent metals [3,20]. In this respect, the available data on c-$Zn_2P_4O_{12}$ are contradictory [2,21,22]. We gave some consideration to this problem in an earlier work [23]; as this property has great practical significance, that study has now been extended by some new observations.

Attention was also focussed on investigating the recrystallization of the products of incongruent melting of the cyclo-tetraphosphate, as this process turns out to be a promising method [24] for synthesis of the binary products.

EXPERIMENTAL

The starting $Zn(H_2PO_4)_2 \cdot 2H_2O$ was thermoanalysed first under dynamic—non-isothermal—conditions (TA) using a low heating rate (2.5 °C min^{-1}), and then under quasi-isothermal quasi-isobaric conditions (Q-TA). The measurements were carried out using a Derivatograph Q-1500 apparatus (MOM Budapest, system by F. Paulik, J. Paulik and L. Erdey) and various types of platinum crucible as sample carriers (Figs. 1 and 2). These crucibles allow retention of the water released at various pressures [18]: in the labyrinth arrangement (D) the water vapour pressure is close to 100 kPa; in the crucible with a lid (C) it is 20 kPa; in the open crucible (B) it is 5 kPa; and in the multi-plate crucible (A) it is almost negligible (1 kPa).

On the basis of the TA and Q-TA results, larger calcinate samples for analysis were then prepared in an electric furnace (Type L 112.2, VEB Frankenhausen, G.D.R.). The samples to be calcined were placed in special vessels corresponding, as regards the water vapour pressure, to crucibles (A) and (D) above. The starting phosphate was first calcined at various temperatures (10 °C steps) within the range 130–360 °C, with a heating rate corresponding to that of TA (2.5 °C min^{-1}). The calcinates were analysed by thin-layer chromatography (TLC) [25], IR spectroscopy [26] (Perkin–Elmer 684 IR spectroscopy apparatus), X-ray diffraction analysis [27,28] (HZG-4 apparatus, G.D.R.) and electron microscopy (Tesla BS 300, C.S.S.R.). The calcinates were also extracted using acetone, water, and 0.3 M HCl [29]. The extractions allowed determination of the temperature ranges within which the individual intermediates persist, particularly $ZnH_2P_2O_7$ and c-$Zn_2P_4O_{12}$.

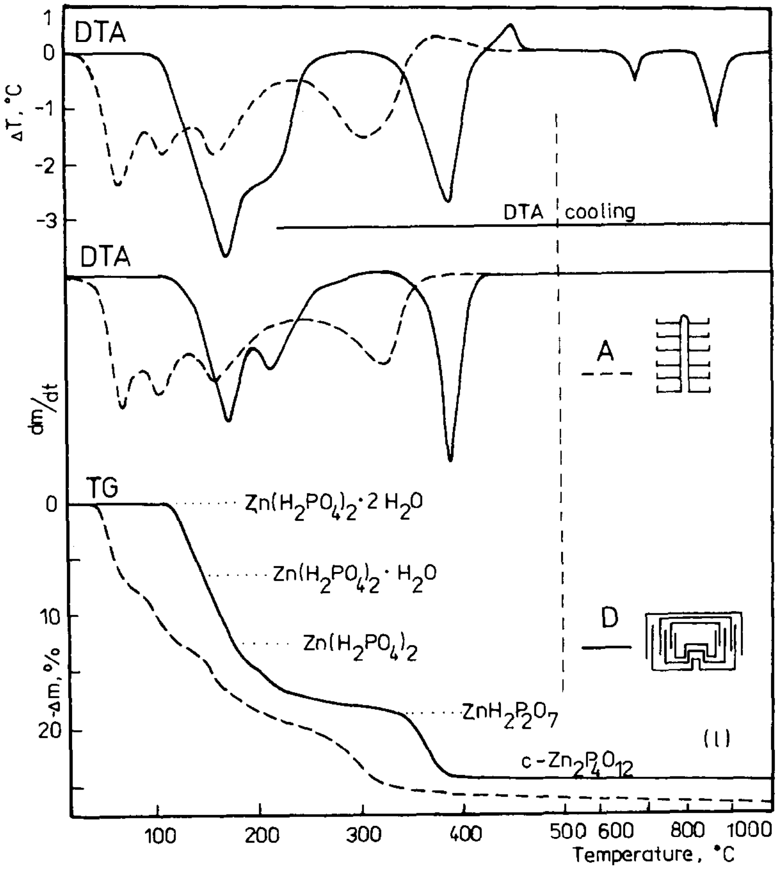

Fig. 1. Simultaneous TG, DTG and DTA curves of $Zn(H_2PO_4)_2 \cdot 2H_2O$ traced under non-isothermal (dynamic) conditions. Apparatus, Derivatograph Q-1500; temperature increase, 2.5 °C min^{-1}; sample weight, 700 mg; standard, α-Al_2O_3. Sensitivity of the balance: TG, 200 mg; DTA and DTG, $\frac{1}{3}$. Atmosphere, air. A, Multi-plate crucible, $pH_2O(g) = 1$ kPa; D, labyrinth crucible, $pH_2O(g) = 100$ kPa.

The solid extraction residues were boiled with dilute HCl (1 : 1) until dissolution, and analysed by the AAS method to determine the ZnO/P_2O_5 ratio. The calcinations were then repeated at 300 and 350 °C for various time periods (up to 500 min) using either the starting $Zn(H_2PO_4)_2 \cdot 2H_2O$ or the intermediates $Zn(H_2PO_4)_2$ and $ZnH_2P_2O_7$. As it is to be expected that any industrial production of c-$Zn_2P_4O_{12}$ will start from a mixture of zinc oxide, carbonate or hydroxide and phosphoric acid [30], we also investigated the kinetics of formation of the product by calcination of these mixtures.

The thermogravimetric (TG) curves from TA and the kinetic curves obtained from the calcination experiments were submitted to a mathematical treatment [31]. The validity of the individual kinetic models of the heterogeneous reactions comprising the condensation reaction by which

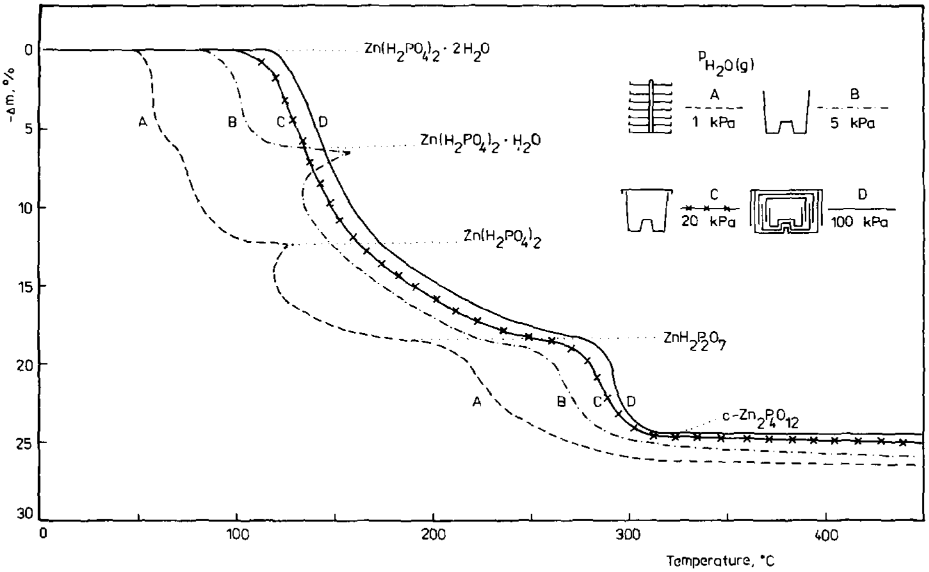

Fig. 2. Thermogravimetric curves of $Zn(H_2PO_4)_2 \cdot 2H_2O$ traced under quasi-isothermal, quasi-isobaric conditions. Apparatus, Derivatograph Q-1500; sample weight, 600 mg; decomposition rate, 0.4 mg min^{-1}; atmosphere, air. A, Multi-plate crucible, $pH_2O(g) = 1$ kPa; B, open crucible, $pH_2O(g) = 5$ kPa; C, crucible with a lid, $pH_2O(g) = 20$ kPa; D, labyrinth crucible, $pH_2O(g) = 100$ kPa.

c-$Zn_2P_4O_{12}$ is formed was evaluated on the basis of statistical characteristics [32].

The thermal stability of the prepared [30] and purified [29] c-$Zn_2P_4O_{12}$ was examined by high-temperature differential thermal analysis (DTA) using a VDTA 8M2 apparatus (the 'Kiev' system, constructed by the Institute of Metal Physics of the Academy of Sciences of the Ukrainian S.S.R.). The atmosphere in the chamber of the apparatus consisted of either dry or wet helium (0.1 MPa He contained about 2 mg water vapour per dm^3 He). The weight changes accompanying calcination of the samples were determined by thermogravimetry using a Derivatograph Q-1500 apparatus and an atmosphere of wet argon. The DTA products were analysed by the same methods as mentioned above. The calcination processes were followed by means of a high-temperature microscope. The c-$Zn_2P_4O_{12}$ samples were also calcined in the electric furnace at various temperatures, and their modification transformation followed by means of X-ray diffraction analysis and density measurements. With the products of incongruent melting we also followed the conditions of thermal recrystallization, the temperatures and heats being determined by DTA and DSC techniques (DTA 1700/DSC Mode Perkin–Elmer) [33].

RESULTS AND DISCUSSION

Thermal analysis of $Zn(H_2PO_4)_2 \cdot 2H_2O$

A simplified mechanism for the reactions of thermal preparation of c-$Zn_2P_4O_{12}$ from $Zn(H_2PO_4)_2 \cdot 2H_2O$ is expressed in eqns. (1)–(4).

$$Zn(H_2PO_4)_2 \cdot 2H_2O = Zn(H_2PO_4)_2 \cdot H_2O + H_2O \tag{1}$$

$$Zn(H_2PO_4)_2 \cdot H_2O = Zn(H_2PO_4) + H_2O \tag{2}$$

$$Zn(H_2PO_4)_2 = ZnH_2P_2O_7 + H_2O \tag{3}$$

$$2ZnH_2P_2O_7 = \text{c-}Zn_2P_4O_{12} + H_2O \tag{4}$$

The results of dynamic (non-isothermal) TA of starting phosphate with a low heating rate (2.5 ° C min^{-1}) carried out with crucibles of two types (Fig. 1) showed that water vapour pressure has a distinct effect on the course of the individual reactions. In the multi-plate crucible, in which the water vapour pressure is practically negligible, the first molecule of water of crystallization (reaction (1)) has already been released at 50 ° C (A). In the labyrinth crucible, in which the water vapour pressure approaches atmospheric pressure, the same process takes place at 125 ° C (D). There is also a difference between the temperatures of the beginning of release of the first molecule of constitutional water (reaction (3)) (130 ° C in the multi-plate and the labyrinth crucible, respectively and 180 ° C). The temperature difference for release of the second molecule of constitutional water (reaction (4)) is even greater (220 ° C and 340 ° C, respectively). The DTA curve for the labyrinth crucible also shows a small exothermic effect corresponding to crystallization of amorphous c-$Zn_2P_4O_{12}$ at 450 ° C. Two endothermic effects appear at 670 ° C and 810 ° C. These effects are not accompanied by any perceptible mass change; as is shown below, one is due to the modification change and the other to the melting of c-$Zn_2P_4O_{12}$. (Under these atmospheric conditions the melting is incongruent and the melt formed slowly solidifies on cooling without showing the corresponding exothermic effect of solidification: see the DTA curve of cooling.) Dynamic TA also revealed a difference in the total change of sample mass. With the labyrinth arrangement (D) the mass decrease was 24.4%, which corresponds precisely to the liberation of four water molecules from the starting phosphate with formation of c-$Zn_2P_4O_{12}$; the mass did not change throughout the temperature region of its subsequent existence (400–810 ° C). With the multi-plate crucible the decrease was higher even within the interval 350–400 ° C (up to 2%) and this difference increased slightly up to 810 ° C.

The thermal analysis under quasi-isothermal, quasi-isobaric conditions was expected to contribute to the elucidation of some of the above-mentioned discrepancies. The TG curve (Fig. 2) obtained with the multi-plate crucible (A) distinctly differentiates between the processes of liberation of the individual water molecules from the starting phosphate (1, 2), the temperatures for the start of release being 50 °C, 70 °C, 125 °C and 195 °C. Above 125 °C the first condensation reaction begins (reaction (3)), giving $ZnH_2P_2O_7$, with formation of nuclei. This takes place at a temperature higher than that of the proper reaction (i.e. at a higher energy content of the compound). Once sufficient nuclei have been formed, the equilibrium is re-established, and the reaction proceeds at the chosen decomposition rate (0.4 mg min^{-1}) and at a temperature corresponding to the actual water vapour pressure (the temperature decreases down to 120 °C). In the open crucible (B, 5 kPa) this effect is already significant soon after the release of the first molecule of water of crystallation. The two subsequent processes, liberation of two molecules of water of crystallization and of one molecule of constitutional water, then practically overlap, and cannot be distinguished by examining the course of the TG curve. The same is true, to a lesser extent, in the case of the crucible with a lid (C, 20 kPa). In the case of the labyrinth crucible (D, 100 kPa), the temperature is not lowered any further during these processes, but differentiating between them using the Q-TG curve is even more difficult. This can be attributed to melting of the starting phosphate in its own water of crystallization. In the multi-plate crucible, from which the liberated water vapour escapes almost immediately, the calcined particles are covered only with a layer of a certain porosity. The impermeability of this layer is increased in the open crucible (B), where the sample becomes almost paste-like. The sample becomes similarly paste-like in the C and D crucibles, from which the liberated water escapes with difficulty. Formation of the first condensation product, $ZnH_2P_2O_7$, was detected in all the crucibles by instrumental analytical methods (IAM), and its composition, molecular structure and amorphous character proved. It can therefore be presumed that in the case of the crucible with higher water vapour pressure, the surface layer of the paste becomes porous only at the moment of formation of the first small amounts of $ZnH_2P_2O_7$ therein; and that only after this perforation is it possible for further water to be liberated from the sample and for the second and third reactions, (2) and (3), to begin. Again the equilibrium is re-established, and the reaction proceeds at the chosen decomposition rate at a temperature corresponding to the actual water vapour pressure. In the crucibles with lower water vapour pressure (A, B and, to a certain extent, C), $ZnH_2P_2O_7$ is partially split into hydrogenphosphate and phosphoric acid, which then condense independently, with the formation of $Zn_2P_2O_7$ and higher polyphosphoric acids as side products and the evaporation of some of the phosphoric acid. The overall mass decrease at lower water vapour pressures is therefore greater than the theoretical value corresponding to liberation of four water molecules from $Zn(H_2PO_4)_2 \cdot 2H_2O$ (24.4%). (This value corresponds to the labyrinth crucible with a water vapour pressure of 100 kPa.) All the processes mentioned affect the second condensation reaction (reaction (4)), formation of c-

$Zn_2P_4O_{12}$, which, depending on the water vapour pressure, begins at 195 °C (A), 220 °C (B), 230 °C (C) and 265 °C (D). At water vapour pressure of 100 kPa (D), the reaction clearly leads to an equilibrium, and the condensation of the main part of the product takes place within a relatively narrow temperature interval at about 290 °C. In this case, the degree of conversion of the calcinate to c-$Zn_2P_4O_{12}$ (determined after completion of Q-TA) reached its highest value (up to 97%). In the crucibles with lower water vapour pressure the degree of conversion was distinctly lower (e.g. 80%, A) and did not increase with increasing temperature.

PREPARATION OF c-$Zn_2P_4O_{12}$

The mass decreases of the samples of $Zn(H_2PO_4)_2 \cdot 2H_2O$ calcined in the electric furnace under conditions corresponding to dynamic TA are presented in Fig. 3a for two different sample carriers. The temperature regions of the existence of $Zn(H_2PO_4)_2$, $ZnH_2P_2O_7$ and c-$Zn_2P_4O_{12}$ were characterized by extraction of the calcinates with acetone, water, and 0.3 M HCl

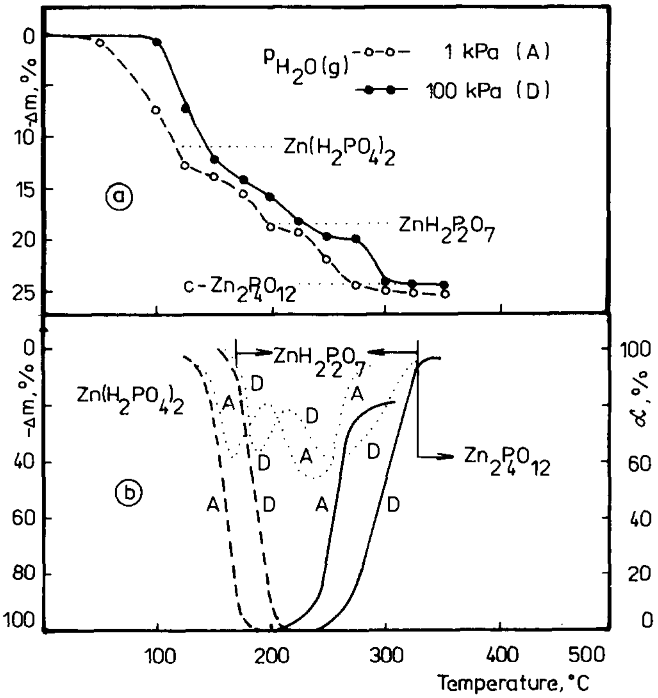

Fig. 3. a, Mass decreases of the $Zn(H_2PO_4)_2 \cdot 2H_2O$ samples calcined in the electric furnace (2.5 °C min^{-1}, $pH_2O(g) = 1$ kPa or 100 kPa). b, Extraction experiments on calcinates of $Zn(H_2PO_4)_2 \cdot 2H_2O$. Weight changes determined by extraction: ······, acetone; — — —, water; ———, 0.3M HCl. α is the degree of conversion with respect to c-$Zn_2P_4O_{12}$.

(Fig. 3b). It is possible to extract a part of the phosphoric component from $ZnH_2P_2O_7$ with acetone, the residue undergoing a topochemical transition to $Zn_2P_2O_7$. (The latter compound is insoluble in acetone)

$$2ZnH_2P_2O_7 = Zn_2P_2O_7 + H_4P_2O_7 \qquad (5)$$

The courses of the extraction curves (Fig. 3b) are not, however, as unambiguous as in the case of the corresponding intermediates of other divalent metals [14–17]. At about 170 °C or 190 °C the portion of extractable phosphoric component is rapidly decreased, and it does not return to the value corresponding to the original portion extractable from $ZnH_2P_2O_7$ until a temperature higher by 50 °C. It is difficult to account for this observation. It can hardly be presumed that the intermediate undergoes a transient change to the form of a phosphate condensed to a higher degree, which would be more resistant to extraction. The explanation could lie in the crystallization of the $ZnH_2P_2O_7$ intermediate. This compound appears in an amorphous form at first and is less resistant to extraction, whereupon it is transformed to a more stable crystalline form. As soon as it begins to undergo the further condensation reaction (reaction (4)), however, its structure is disturbed, and its extraction becomes easier again. More distinct portions of c-$Zn_2P_4O_{12}$ begin to appear in the calcinate above 240 °C (at the low water vapour pressure) and 270 °C (at 100 kPa), these portions being stabilized at the values of 81.5% (at 285 °C) and 97.6% (at 335 °C), respectively. (These findings agree with the conclusions of TA.)

The temperatures of 300 °C (1 kPa water vapour pressure) and 350 °C (100 kPa) were chosen for the investigation of the kinetics of formation of c-$Zn_2P_4O_{12}$. The results of this investigation are given in Fig. 4. For 100 kPa water vapour pressure in the calcinate area, more than 97% of the calcinate

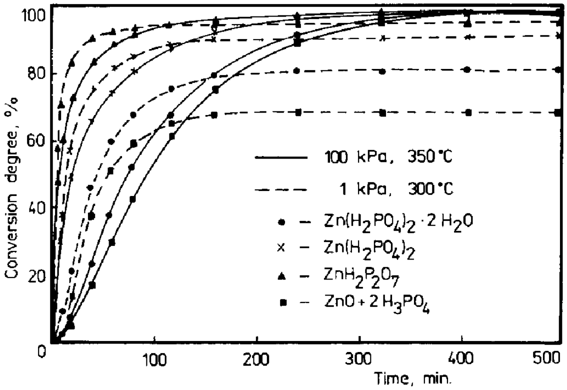

Fig. 4. Dependence of the degree of conversion of the starting zinc(II) phosphates $Zn(H_2PO_4)_2 \cdot 2H_2O$ (●), $Zn(H_2PO_4)_2$ (×), $ZnH_2P_2O_7$ (▲) or starting mixture $ZnO + 2H_3PO_4$ (■) to c-$Zn_2P_4O_{12}$ on the calcination time, for the calcination temperatures 300 °C ($pH_2O(g) = 1$ kPa) (— — —) and 350 °C ($pH_2O(g) = 100$ kPa) (———).

was converted into c-$Zn_2P_4O_{12}$ within 500 min of calcination with all the starting compounds, even the $ZnO + H_3PO_4$ mixture. For 1 kPa water vapour pressure, the values were perceptibly lower. The highest degree of conversion at this water vapour pressure, and hence the smallest difference from the result at 100 kPa, was achieved using $ZnH_2P_2O_7$ as the starting compound. This indicates that the side reactions leading to the reduction in product yield occur principally during the formation of $ZnH_2P_2O_7$.

Mathematical treatment of the kinetic curves (Fig. 4) and the TG curves from dynamic TA (Fig. 1) revealed that diffusion is the controlling process of the condensation reaction. This is best expressed by the anti-Jander equation

$$\left((1+\alpha)^{1/3} - 1\right)^2 = kt$$

for so-called countercurrent diffusion [31,32]. In this way it was possible to confirm the results obtained by electron microscopy, which indicated distinct porosity of the intermediate $ZnH_2P_2O_7$ formed. Taking into account all the circumstances, however, we can state that the condensation reaction, formation of c-$Zn_2P_4O_{12}$, probably leads to an equilibrium (especially in the labyrinth crucible), but that the course of the reaction is affected by the porosity of the upper layer of the calcinate which forms on the nuclei.

As shown in Fig. 1, dynamic TA using the Derivatograph Q-1500 registered two further endothermic effects above the temperatures for the completion of the process of c-$Zn_2P_4O_{12}$ production. The first of these effects started at 670 °C, and the second at 810 °C. The pure cyclo-tetraphosphate prepared was therefore submitted to individual thermal analysis and calcination, and analysis was performed on the calcinates which were prepared at temperatures within the range 500–850 °C. The results confirmed that the modification change from α_1-c-$Zn_2P_4O_{12}$ to α_2-c-$Zn_2P_4O_{12}$ occurs at 670 °C, and were in agreement with the findings of Katnack and Hummel [21], except that these authors observed the change at temperatures lower by 30–50 °C. Nirsa et al. [2] have described the same change as the change of the mixture formed by the products of two modifications (α_1 and α_2) on the product of α-modification. On the basis of the results obtained in our laboratory, we suggest that the first mechanism for the change ($\alpha_1 \rightarrow \alpha_2$) is more likely, though X-ray diffraction analysis has not confirmed this conclusively. We have used DTA/DSC to determine a heat for this modification change of 19.5 J g^{-1}. The change was also recorded by observing the density of c-$Zn_2P_4O_{12}$ samples calcinated at the various temperatures. Figure 5 shows the density values determined experimentally by the pycnometric method. A step change of density of approximately 0.35 g cm^{-3} occurs within the temperature range 650–700 °C, when the density changes, approximately, from 3.5 g cm^{-3} to 3.15 g cm^{-3}. The first density value corresponds to α_1-modification of c-$Zn_2P_4O_{12}$, and the second to α_2-modification.

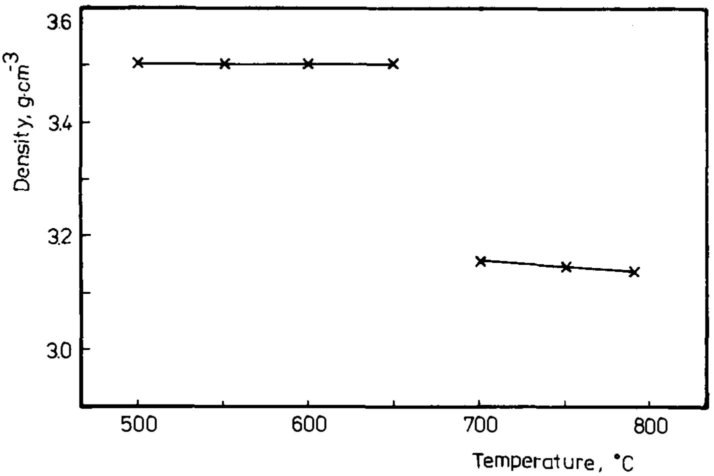

Fig. 5. Dependence of the density of c-$Zn_2P_4O_{12}$ on the calcination temperature.

DTA of c-$Zn_2P_4O_{12}$ (VDTA 8M2 apparatus) measured under dry He showed distinct endothermic effects of melting (Fig. 6a). With c-$Zn_2P_4O_{12}$, this occurred at 810 °C. With c-$Zn_2P_4O_{12}$, an endothermic effect corresponding to modification change was also noticed at 680 °C. DTA of cooling indicated a corresponding exothermic effect of solidification of the melt of cyclo-tetraphosphate. Repeated DTA of heating of the same sample showed the respective endothermic effect of melting at the same temperatures. IAM confirmed that after DTA the samples contained only the microcrystalline cyclo-tetraphosphates (α_2-modification). Hence, these substances only undergo congruent melting under these conditions.

Figure 6b gives the DTA curves for c-$Zn_2P_4O_{12}$ in an atmosphere of wet helium. The melting takes place at the same temperatures as in the dry atmosphere. The cooled samples were glassy products. Therefore, practically no effects were observed which would correspond to their solidification during the DTA cooling. IAM confirmed that they were composed of molecules of higher linear phosphates and were non-crystalline and amorphous in character. Their chains are broken (and, hence, their existence ended) simply by the presence of water molecules in the atmosphere of the chamber

$$\frac{n}{4}c\text{-}Zn_2P_4O_{12} + H_2O \rightarrow Zn_{n/2}H_2P_nO_{3n+1} \qquad (6)$$

Repeated heating of the Zn glasses showed exothermic effects from 535 °C upwards, the latter being less distinct. IAM showed that these effects correspond to crystallization of the glasses with formation of the original cyclo-tetraphosphates and release of the end groups of water molecules.

$$Zn_{n/2}H_2P_nO_{3n+1} \rightarrow \frac{n}{4}c\text{-}Zn_2P_4O_{12} + H_2O \qquad (7)$$

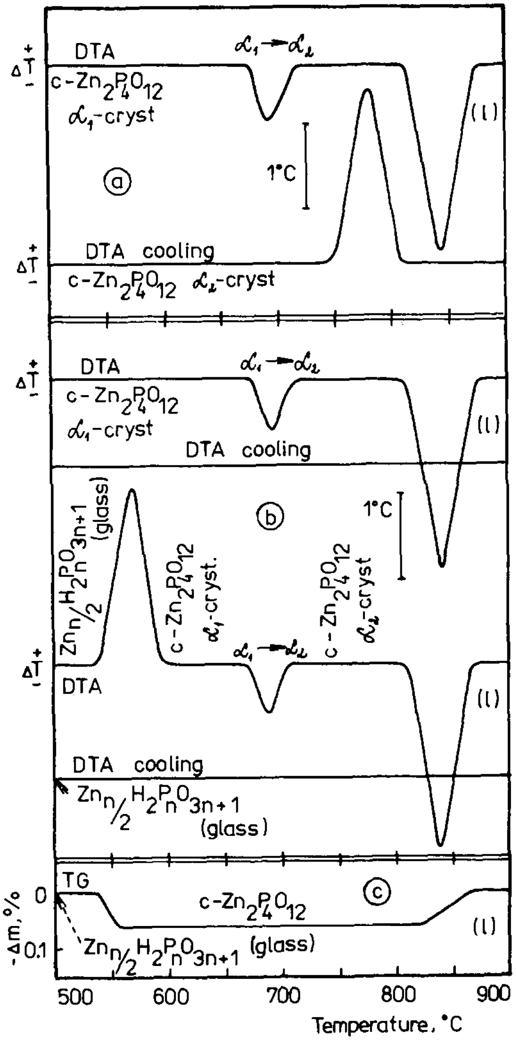

Fig. 6. Determination of the thermal stability of c-$Zn_2P_4O_{12}$ and $Zn_{n/2}H_2P_nO_{3n+1}$(glass) by means of thermal analysis. a, DTA curves of c-$Zn_2P_4O_{12}$ in dry helium (0.1 MPa); b, DTA and c, TG curves of c-$Zn_2P_4O_{12}$ and $Zn_{n/2}H_2P_nO_{3n+1}$(glass) in (0.1 MPa) wet helium (DTA) and wet argon (TG). A VDTA 8M2 apparatus, heating (or cooling) rate 40 °C min^{-1}, sample weight 100 mg, standard α-Al_2O_3 and molybdenum crucible were used for DTA; a Derivatograph Q-1500 apparatus, heating rate 20 °C min^{-1}, sample weight 2000 mg, balance sensitivity 20 mg and platinum crucible were used for TG.

Participation of water in the process was confirmed by TG using a Derivatograph Q-1500 apparatus (Fig. 6b). A weight decrease was recorded during recrystallization of large samples at high sensitivity of TG (transformation of the glasses into cyclo-tetraphosphate (7)). Melting of the cyclo-tetraphosphates in the wet atmosphere was accompanied by comparable increases of sample weight corresponding to the formation of higher linear phosphates.

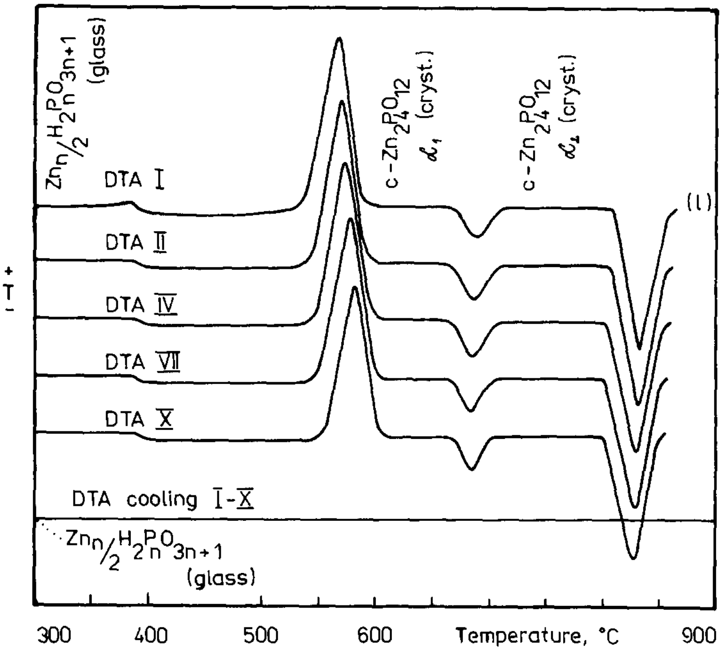

Fig. 7. Repeated DTA curves of vitreous (glass) $Zn_{n/2}H_2P_nO_{3n+1}$. DTA 1700/DSC Mode Perkin–Elmer apparatus; sample weight, 15 mg; temperature increase, 20 °C min^{-1}; platinum crucible (open); atmosphere, air.

The weight change was 0.06%, which corresponds to $n > 300$ in the formula $Zn_{n/2}H_2P_nO_{3n+1}$. The results obtained show that the congruence or non-congruence of the melting of c-$Zn_2P_4O_{12}$ is related to the melting conditions, i.e. whether the atmosphere of the melt space is dry or wet. This explains the discrepancies in data reported in the literature with regard to this problem. The authors of refs. 1–4 report melting of c-$Zn_2P_4O_{12}$ at temperatures 50–60 °C higher, and do not deal with the problem of the congruence or non-congruence at all. The authors of ref. 22 admit only congruent melting at 830 °C, whereas other authors have described the transfer of α_1-modification of c-$Zn_2P_4O_{12}$ as so-called high-temperature α-modification, expressed by the formula of $Zn(PO_3)_2$, at 790 °C.

Under conditions of normal air atmosphere, DTA of heating and cooling of the same sample of $Zn_{n/2}H_2P_nO_{3n+1}$ was performed ten times in total, using the DTA 1700/DSC instrument. Figure 7 shows curves for DTA of $Zn_{n/2}H_2P_nO_{3n+1}$ (curve I); and for DTA of the same sample repeated once (II), four times (IV), seven times (VII), and ten times (X). Values were determined for the temperatures of modification transfer (T_{modif}), temperatures of melting (T_{melt}), temperatures of softening of the vitrial product (T_g), temperatures of the start of recrystallization (T_R), temperatures of maximum exothermic recrystallization effect (T_{max}), and for heats corresponding to exothermic recrystallization effects, endothermic effects of modification

TABLE 1

Values of parameters related to processes occurring during repeated DTA $Zn_{n/2}H_2P_nO_{3n+1}$

Numbers of repeats of recrystallization and melting	T_g (°C)	T_R (°C)	T_{max} (°C)	$-\Delta H$ of recrystallization (J g^{-1})	Yield of recrystallization (%)	T_{modif} (°C)	ΔH of modification (J g^{-1})	T_{melt} (°C)	ΔH of melting (J g^{-1})
I	380	535	558	137	90.5	670	19.5	810	92
II	380	537	563	127	88.3	672	18.9	807	93
IV	385	542	568	121	84.7	669	17.1	804	89
VII	390	548	578	115	78.5	670	15.7	801	88
X	390	555	586	110	71.2	671	14.0	800	85

transfer, and melting. The yields of recrystallization of vitrial product to c-$Zn_2P_4O_{12}$ were also determined, by analytical means [29]. All the values obtained are summarized in Table 1. On repeated melting and recrystallization, the content of c-$Zn_2P_4O_{12}$ in the sample after recrystallization decreases gradually, by as much as 70% in the case of ten repeats. The residue of the sample remains in the form of the higher linear phosphate.

$$Zn_{n/2}H_2P_nO_{3n+1} \rightarrow (1-x)\frac{n}{4}\text{c-}Zn_2P_4O_{12} + (1-x)H_2O + xZn_{n/2}H_2P_nO_{3n+1} \qquad (8)$$

It is probably for this reason that the heat of recrystallization decreases slightly with increasing repeats of the melting and recrystallization process, in contrast to the temperature of the start of recrystallization, which increases. The c-$Zn_2P_4O_{12}$, which arises by recrystallization is at first in the α_1-modification, and changes to the α_2-modification at approximately 670 °C. The temperature of this modification change is almost independent of the number of repeats of the melting and recrystallization process. However, the values of the heat corresponding to the endothermic effect of this change decrease slightly. This is again in agreement with the decreasing content of c-$Zn_2P_4O_{12}$ in the recrystallization sample. The temperature and the heat of sample melting change only slightly, decreasing with increasing numbers of repeats of melting and recrystallization. In the first part of the DTA curve for heating of vitrial $Zn_{n/2}H_2P_4O_{3n+1}$, softening of the sample (T_g) was observed within the temperature range 380–390 °C.

CONCLUSIONS

The processes which take place during calcination of $Zn(H_2PO_4)_2 \cdot 2H_2O$ and bring about the formation of c-$Zn_2P_4O_{12}$, as well as the processes which take place during calcination of c-$Zn_2P_4O_{12}$ and determine its thermal stability, can be expressed by the following scheme.

$$\begin{aligned}
&\mathrm{Zn(H_2PO_4)_2\cdot 2H_2O} \xrightarrow[-2\mathrm{H_2O}]{115\text{–}170\,^\circ\mathrm{C}\ *} \mathrm{Zn(H_2PO_4)_2} \xrightarrow[-\mathrm{H_2O}]{170\text{–}260\,^\circ\mathrm{C}\ *} \mathrm{ZnH_2P_2O_7}\\
&\xrightarrow[-\mathrm{H_2O}]{260\text{–}330\,^\circ\mathrm{C}\ *} \tfrac{1}{2}\text{c-}\mathrm{Zn_2P_4O_{12}}(\text{amorph.}) \xrightarrow{400\,^\circ\mathrm{C}\ *} \tfrac{1}{2}\alpha_1\text{-c-}\mathrm{Zn_2P_4O_{12}}(\text{cryst.})\\
&\xrightarrow{670\,^\circ\mathrm{C}} \tfrac{1}{2}\alpha_2\text{-c-}\mathrm{Zn_2P_4O_{12}}(\text{cryst.}) \xrightarrow[+\frac{2}{n}\mathrm{H_2O}]{810\,^\circ\mathrm{C}\ **} \frac{2}{n}\mathrm{Zn}_{n/2}\mathrm{H_2P}_n\mathrm{O}_{3n+1}(\mathrm{l})\\
&\xrightarrow{810\to 25\,^\circ\mathrm{C}\ **} \frac{2}{n}\mathrm{Zn}_{n/2}\mathrm{H_2P}_n\mathrm{O}_{3n+1}(\text{glass})\\
&\xrightarrow[-\frac{2}{n}\mathrm{H_2O}]{535\,^\circ\mathrm{C}\ **} x(\alpha_1\text{-c-}\mathrm{Zn_2P_4O_{12}}(\text{cryst.})) + (1-x)\frac{2}{n}\mathrm{Zn}_{n/2}\mathrm{H_2P}_n\mathrm{O}_{3n+1}(\text{glass})\\
&\xrightarrow{670\,^\circ\mathrm{C}\ **} x(\alpha_2\text{-c-}\mathrm{Zn_2P_4O_{12}}(\text{cryst.})) + (1-x)\frac{2}{n}\mathrm{Zn}_{n/2}\mathrm{H_2P}_n\mathrm{O}_{3n+1}(\text{glass})\\
&\xrightarrow[+x\frac{2}{n}\mathrm{H_2O}]{800\text{–}810\,^\circ\mathrm{C}\ **} \frac{2}{n}\mathrm{Zn}_{n/2}\mathrm{H_2P}_n\mathrm{O}_{3n+1}(\mathrm{l})
\end{aligned} \tag{9}$$

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* Water vapour pressure ≈100 kPa.

** Wet normal air atmosphere.

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