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STUDY OF THERMAL DEHYDRATION OF $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$

M. TROJAN and D. BRANDOVÁ

Institute of Chemical Technology, Lenin Square 565, Pardubice 53210 (Czechoslovakia)

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ABSTRACT

The dehydration and condensation reactions that take place during calcination of $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$ were followed by means of thermal analyses under non-isothermal (dynamic) and quasi-isothermal–isobaric conditions. Isothermal calcination of the starting binary dihydrogenphosphate was carried out in an electric oven at various temperatures and water vapour pressures. The reaction intermediates and products obtained were analysed by instrumental analytical methods and extraction experiments with solutions of water, acetone and 0.3 M HCl. The results indicate the effects of varying water vapour pressure on the courses, rates and yields of the condensation reactions and on the formation of the main product of interest, binary cyclo-tetraphosphate (tetrametaphosphate) $c\text{-}MnMgP_4O_{12}$.

INTRODUCTION

Cyclo-tetraphosphates (tetrametaphosphates) [1] of general formula $c\text{-}Me_2^{II}P_4O_{12}$ (where Me^{II} is for example, Zn, Mn, Co, Mg, Cd or Ni) can be prepared by thermal dehydration of dihydrogenphosphates of bivalent metals. In our laboratory they have been tested as microadditives to fertilizers with long-term action [2], and some of them have been used as special thermostable inorganic pigments: luminescent [3,4], anti-corrosive [5,6] and coloured [7,8]. Studies have been made of their synthesis using thermal analysis (TA) methods, especially under quasi-isothermal–isobaric conditions [9–12]. Recently, we have been focusing on the preparation of binary cyclo-tetraphosphates, i.e. species in which a part of the bivalent (non-ferrous) metal cation is substituted with cheaper cations of alkaline earth metals (mainly Mg and Ca). The cost of the product is thereby reduced and the application qualities are improved. Such products have not previously been described in the literature (nor have they been mentioned in recent reviews of the literature [13–15]). Our latest works have shown that binary cyclo-tetraphosphates containing magnesium do exist [16,17]. Their general formula is $c\text{-}Me_{2-x}^{II}Mg_xP_4O_{12}$, with x as a rule assuming any valve within the possible range (i.e. $x \in (0; 2)$) [18]. The starting raw material for their

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preparation is a suitable mixture containing the compounds of magnesium (with a volatile anion) and the appurtenant bivalent metal with phosphoric acid. The final product is obtained from this mixture by thermal means [16]. In laboratory experiments aimed at determining the basic conditions of the synthesis and elucidating the mechanism of the dehydration and condensation reactions by which the binary product is formed it is, however, preferable to use binary dihydrogenphosphate in the hydrated form, prepared in advance. The present paper surveys results obtained from the thermal treatment of $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$.

EXPERIMENTAL

The starting binary dihydrogenphosphate $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$ (light pink crystals) was prepared in our laboratory by crystallization from a solution containing Mn^{2+}, Mg^{2+} and PO_4^{3-} ions in stoichiometric quantities, thickened at 60 ° C. The quality of the product was confirmed by atomic absorption spectrometry (AAS) and X-ray diffraction analysis, and its morphology by electron microscopy.

In order to elucidate the mass and energy transformations that occur during calcination, the sample was thermoanalysed by the classical dynamic method (i.e. non-isothermal) using a Derivatograph C apparatus (MOM, Budapest). The measurements were carried out in a labyrinth crucible, under conditions as follows: heating rate, 2 ° C min^{-1}; sample weight, 147.85 mg; sensitivity of TG, 100 mg; of DTA, 2; of DTG, 2; temperature interval, 20–400 ° C. The examination was carried out in the presence of air (see Fig. 1 below).

In order to more clearly distinguish between the individual processes taking place during the calcination, and to follow the effect upon these of varying water vapour pressure, the starting dihydrogenphosphate was submitted to TA under quasi-isothermal, quasi-isobaric conditions (Q-TA) with the same equipment [19–21]. The sample weight was about 150 mg and the decomposition rate chosen was 0.3 mg min^{-1} (calculated for a 100 mg total weight change). The first measurements performed under these conditions used the Derivatograph C apparatus with a crucible with a lid as the sample carrier (Fig. 2 below: heating rate, 1 ° C min^{-1}; sensitivity of DTG, 0.5; of DTA, 2). Thermogravimetric measurements were then performed, under quasi-isothermal–isobaric conditions, using the Derivatograph Q-1500 apparatus (MOM, Budapest) with four different platinum crucible types as carriers of the sample for thermoanalysis (Fig. 3 below): a multi-plate crucible (curve A), an open crucible (B), a crucible with a lid (C), and a six-component labyrinth set (D). This last arrangement (D) allows retention of the water vapour released during calcination of the starting dihydrogenphosphate, so that the partial pressure is maintained at about 100 kPa.

With the other three crucibles (A, B and C), the partial pressure corresponds to approximately 1 kPa (which is negligible), 5 kPa and 20 kPa, respectively.

The results obtained from these Q-TA runs were then made use of in preparation of the condensation products and intermediates by calcination of the starting dihydrogenphosphate in an electric furnace (Type L 112.2, VEB, Frankenhausen, G.D.R.) with a programmable heating rate, Chinoin 10A (Chinotherm, Budapest) at various temperatures (80, 100, 120, ... 600 ° C), under isothermal conditions maintained for 30 min (heating rate, 2 ° C $\min^{-1}$), in a flat corundum pan (corresponding to 1 kPa) and in a composition of corundum crucibles (120 kPa).

On the basis of the results of earlier investigations, various organic and inorganic solvents [21,22] were chosen for extraction of the calcinates. The extraction experiments made it possible to follow the formation and persistence of the individual intermediates, particularly dihydrogendiphosphate and the main product cyclo-tetraphosphate. The samples prepared by calcination in the electric furnace under isothermal conditions were thus extracted using acetone, water and 0.3 M HCl (Fig. 4 below). The extractable phosphate components in acetone (phosphoric or diphosphoric acid) were expressed as the P_2O_5 fraction of the total amount in the calcinate. Thereafter, the calcinates were extracted using water, which dissolves the intermediate $Mn_{0.5}Mg_{0.5}H_2P_2O_7$. The calcinated samples were also extracted using 0.3 M HCl, in which only the final product c-$MnMgP_4O_{12}$ (or c-$Mn_2P_4O_{12}$ and c-$Mg_2P_4O_{12}$) is insoluble.

The starting phosphate and the calcinates were analysed and the individual products of the Q-TA identified using TLC [23,24], IR spectroscopy [25] (Perkin–Elmer 684 IR spectrometer), X-ray diffraction analysis [26,27] (HZG-4 apparatus, G.D.R.) and electron microscopy (Tesla BS 300, C.S.S.R.) techniques. The solid residues from each extraction experiment were also analysed, by the same instrumental analytical methods (IAM). On boiling with dilute (1 : 1) hydrochloric acid, the residues dissolved, and the $Me^{II}O/P_2O_5$ ratios were determined by AAS [28].

RESULTS AND DISCUSSION

Thermal analysis of $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$ *under dynamic conditions*

The thermoanalytical curves for the starting tetrahydrate of binary manganese–magnesium dihydrogenphosphate $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$ (Fig. 1) recorded under dynamic conditions with the labyrinth crucible show that in total five endothermic processes take place. These are always accompanied by mass losses representing, in total, 37.5% of the original mass of the thermoanalysed sample. This agrees very closely with the theoretical mass loss (37.4%) corresponding to the release of all six water

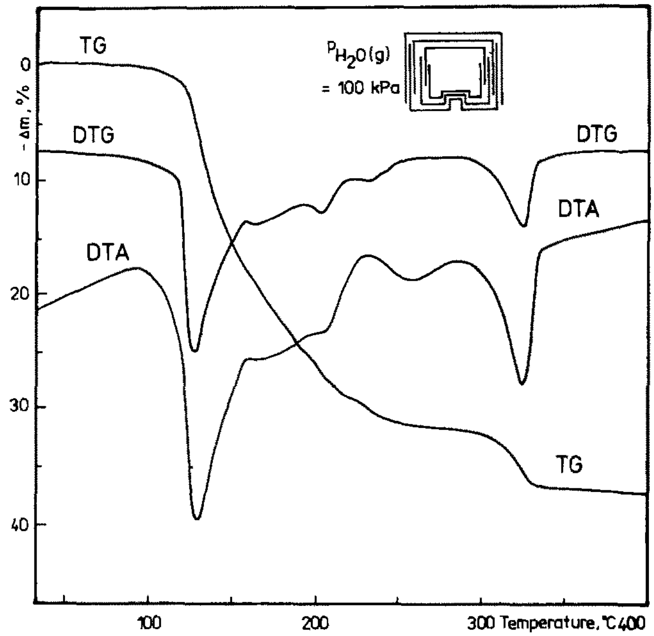

Fig. 1. Simultaneous TG, DTG and DTA curves of $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$ under dynamic (non-isothermal) conditions. Apparatus, Derivatograph C; heating rate, 1° C min^{-1}; sample weight, 149.85 mg; standard, α-Al_2O_3. Sensitivity of the balance: TG, 100 mg; DTA, 2; DTG, 2. Labyrinth crucible; $pH_2O(g) = 100$ kPa; atmosphere, air.

molecules (four of water of crystallization and two of constitutional water) from the starting dihydrogenphosphate. Three water of crystallization molecules are liberated first, in an endothermic process within the temperature interval 120–165 °C (with the maximum at 130 °C). The fourth water of crystallization molecule is released within the temperature interval 165–200 °C, and this is associated with an only slightly distinct endothermic effect. The first molecule of constitutional water is liberated within the temperature interval 200–290 °C. The courses of the TG, DTG and DTA curves show that the release may take place through two closely linked processes (the first within 200–230 °C, the second within 230–290 °C). The second molecule of constitutional water is then released in a distinct endothermic process within the interval 290–330 °C.

Thermal analysis of $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$ under quasi-isothermal–isobaric conditions

Figure 2 shows examples of individual thermoanalytical curves obtained by Q-TA using the Derivatograph C apparatus and a labyrinth crucible as sample carrier, with the vapour pressure in the sample space approaching the surrounding atmospheric pressure, i.e. 100 kPa. The curves are in fairly

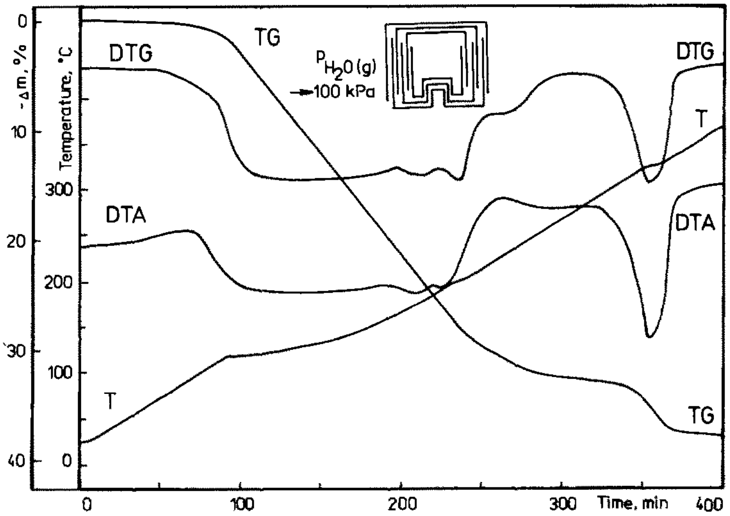

Fig. 2. Simultaneous TG, DTG and DTA curves of $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2\cdot 4H_2O$ under quasi-isothermal, quasi-isobaric conditions. Apparatus, Derivatograph C; decomposition rate, 0.3 mg min^{-1}; heating rate, 1° C min^{-1}; sample weight, 150 mg. Sensitivity of the balances; TG, 100 mg; DTA, 2; DTG, 0.5. Labyrinth crucible; atmosphere , air.

good agreement with the processes and temperature intervals recorded using the same crucible under dynamic conditions with a slow heating rate (Fig. 1). However, release of all four water of crystallization molecules seems to take place in one continuous process within the temperature interval 120–190 ° C. Further measurements under quasi-isothermal–isobaric conditions were then carried out with four different crucible types as carriers of the thermoanalysed sample, this time using the Derivatograph Q-1500 apparatus.

Labyrinth crucible

Figure 3 (curve D) shows the results of a thermogravimetric run starting with $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2\cdot 4H_2O$ using the labyrinth crucible, i.e. at vapour pressures approaching 100 kPa. The course of the curve shows that under these conditions all water of crystallization is released in one protracted continuous process within the temperature interval 120–190 ° C. (This temperature interval and the course of the Q-TG curve (D) in Fig. 3 provide some confirmation that all the water contained in the thermoanalysed sample, except for the constitutional water, is really bound as water of crystallization and not only as moisture.) The results are in fairly good agreement with the temperatures for the release of water of crystallization from the simple dihydrogenphosphates of manganese and magnesium ($Mn(H_2PO_4)_2\cdot 2H_2O$, 120 ° C [12]; $Mg(H_2PO_4)_2\cdot 2H_2O$, 130–170 ° C [29]). At 190 ° C the calcinate is the anhydride of the binary dihydrogenphosphate, $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2$. IAM were used to confirm its existence and binary nature.

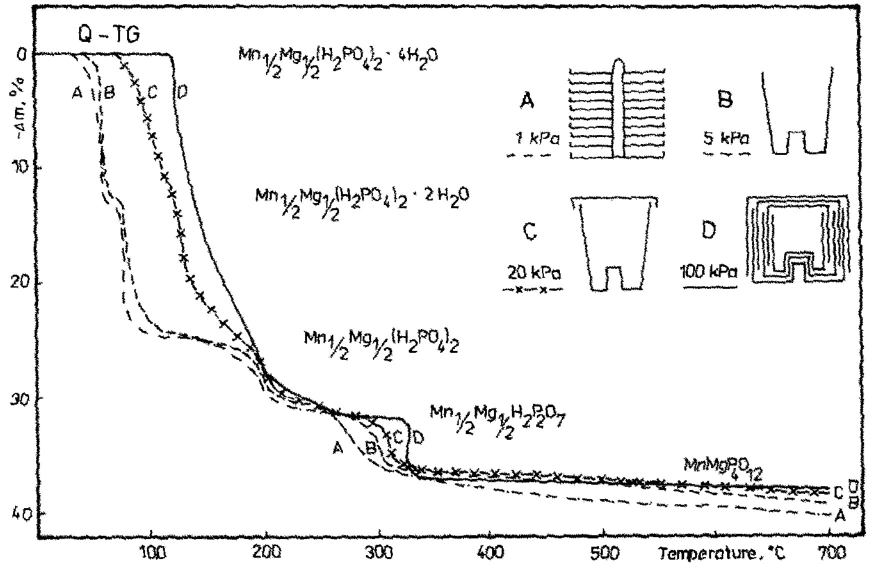

Fig. 3. Thermogravimetric curves of $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$ under quasi-isothermal, quasi-isobaric conditions. Apparatus, Derivatograph Q-1500; decomposition rate, 0.3 mg min^{-1}; sample weight, 200 mg; atmosphere, air. (A) Multiplate crucible, $pH_2O(g) = 1$ kPa; (B) open crucible, $pH_2O(g) = 5$ kPa; (C) crucible with a lid, $pH_2O(g) = 20$ kPa; (D) labyrinth crucible, $pH_2O(g) = 100$ kPa.

The first molecule of constitutional water is released within the temperature interval 190–250 ° C, the principal part of it (about half) being liberated practically isothermally at 190–200 ° C. The first condensation reaction takes place at the same time, forming the intermediate product binary dihydrogendiphosphate $Mn_{0.5}Mg_{0.5}H_2P_2O_7$, as confirmed by IAM. The temperature zone within which this important intermediate forms and persists was also confirmed by experiments in which calcinate samples of starting $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$ (prepared under isothermal conditions in the electric oven) were extracted with acetone (Fig. 4a: interval, 200–260 ° C). This temperature interval lies roughly between (and partly coincides with) the intervals determined by Q-TA [12,29] and by extraction experiments probing for the formation and persistence of the simple dihydrogendiphosphates $MnH_2P_2O_7$ and $MgH_2P_2O_7$ (Fig. 4, b and c). These intervals were found to be 195–305 ° C for $MnH_2P_2O_7$ and 170–390 ° C for $MgH_2P_2O_7$. Comparing the three temperature intervals provides some confirmation that when $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$ is calcinated under these conditions, the first condensed product is really the binary species $Mn_{0.5}Mg_{0.5}H_2P_2O_7$, and not a mixture of the simple products $MnH_2P_2O_7$ and $MgH_2P_2O_7$. (This view was supported not only by IAM results, but also by electron microscope observations of both the calcinates and the solid state residues after extraction with acetone.)

The final process observed is the release of the second molecule of constitutional water connected with the second condensation reaction forming cyclo-tetraphosphate. In the labyrinth crucible this takes place within the temperature interval 250–400 °C, the principal part of it (over 80% by mass) being liberated practically isothermally at 325–330 °C. Above 400 °C, the sample mass remains almost unchanged, the product obtained being binary manganese–magnesium cyclo-tetraphosphate c-$MnMgP_4O_{12}$ (as confirmed by IAM). This product represents a new compound not previously described in the literature, and now protected by a Czechoslovak patent application [30]. Its crystal structure was found to be monoclinic, group $C2/c$, with structural parameters $a = 1.1904(5)$ nm, $b = 0.8408(4)$ nm, $c = 0.9967(4)$ nm, $\beta = 118.92°(2)$, elementary cell volume = 0.8732 nm^3, and density $\rho = 3.006$ g cm^{-3} (calculated) or 3.00 g cm^{-3} (experimental). Comparing the temperature zones of formation (under equivalent conditions) of

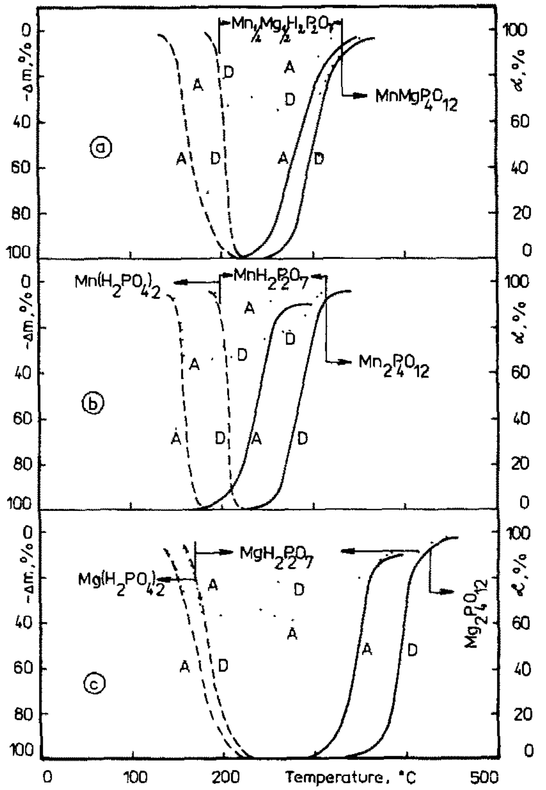

Fig. 4. Extraction experiments on calcinates of $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$, $Mn(H_2PO_4)_2 \cdot 2H_2O$ and $Mg(H_2PO_4)_2 \cdot 2H_2O$. Calcination conditions: heating rate, 2 °C min^{-1}; pH_2O(g), 1 kPa (A) or 100 kPa (D). Weight changes determined by extraction: · · · · · ·, acetone; — —, water; ———, 0.3 M HCl. α is the degree of conversion with respect to the cyclo-tetraphosphates.

the corresponding individual products, c-$Mn_2P_4O_{12}$ and c-$Mg_2P_4O_{12}$, it can be seen that they are somewhat different: the manganese product is formed at temperatures slightly below 300–310 °C, [12], while the magnesium product is formed at rather higher temperatures (390–460 °C) [29].

The extraction experiments with 0.3 M HCl carried out on the calcinates prepared under appropriate conditions in an electric oven (Fig. 4) confirmed these conclusions. At a vapour pressure of nearly 100 kPa during the calcination of the individual starting dihydrogenphosphates ($Mn(H_2PO_4)_2 \cdot 2H_2O$, $Mg(H_2PO_4)_2 \cdot 2H_2O$ and $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$), the first portions of the final products (cyclo-tetraphosphates) begin to appear at 270 °C (Mn), 270 °C (Mn–Mg) and 350 °C (Mg). The final (steady-state) degrees of conversion obtained for the individual calcinates under these conditions were: about 95% for c-$Mn_2P_4O_{12}$ (at 350 °C); above 97% for c-$MnMgP_4O_{12}$ (at 350 °C); and nearly 99% for c-$Mg_2P_4O_{12}$ (at 460 °C).

Multi-plate crucible

Figure 3 (curve A) shows the results of thermal analysis of $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$ under quasi-isothermal–isobaric conditions with the multi-plate crucible, i.e. at negligible water vapour pressure (1 kPa) over the sample. The course of curve A is comparable to the course of curve D (labyrinth crucible) described above. It is different as expected, in as much as the temperature values for individual processes are lower: 80–100 °C lower for the release of water of crystallization, 10–50 °C lower for processes connected with the release of the first molecule of constitutional water, and 10–70 °C lower for processes connected with the release of the second molecule of constitutional water. Curve A is also different in that the water of crystallization is evidently liberated in two steps: the first two molecules within the interval 40–60 °C, the principal part of this process occurring almost isothermally, at 55–60 °C; and the next two molecules within the interval 60–140 °C, the principal part again occurring isothermally, at 75 °C. A further difference lies in a breakage in the Q-TG curve at 190 °C, halfway along the interval corresponding to the release of the first molecule of constitutional water and of dihydrogendiphosphate formation. This provides evidence for partial splitting of the intermediate product—the binary anhydride–under low vapour pressures. These last two differences between the courses of curves A and D (Fig. 3) prove that under conditions of low water vapour pressure the binary intermediate products split to form simple intermediates, i.e. bivalent metals (Mn and Mg) in the form of anhydrides or partial anhydrides. The temperature of release of the first two molecules of water of crystallization from $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$ corresponds very exactly to e.g. that of the liberation of both the molecules of water of crystallization from $Mn(H_2PO_4)_2 \cdot 2H_2O$ [12]. The liberation of the first molecule of constitutional water from binary dihydrogenphosphate, which is divided on the above-mentioned breakage into two comparable parts, can thus be said to be (to some extent at least) similar to the liberation of one molecule of constitutional water from the simple dihydrogenphosphates: from $Mn(H_2PO_4)_2$ (i.e. the first part) [12] and $Mg(H_2PO_4)_2$ (the second part). An intermediate product of dihydrogendiphosphate type is thus formed, although a part of this is a mixture of the simple dihydrogendiphosphates, $MnH_2P_2O_7$ and $MgH_2P_2O_7$. The final difference between the courses of the A and D Q-TG curves involves a steady decrease in the mass of the thermoanalysed sample, even after the theoretical mass loss corresponding to the release of six water molecules (37.4%) has been reached at 350 ° C. (Up to the final temperature of Q-TA at 700 ° C, a further 3% of the sample mass is lost.)

Analysis by IAM of calcinates prepared at various temperatures showed that the mechanism of dehydration and condensation reactions that occurs during the calcination of $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$ at low vapour pressures resembles the equivalent mechanism, described in previous works of ours [9–12], for the comparable calcination of simple dihydrogenphosphates of bivalent metals; and is similar to the mechanism we have observed for the calcination of binary calcium dihydrogenphosphates [31]. At low water vapour pressure a part of the phosphoric component is split away from individual intermediates, to leave hydrogenphosphates. The split-away components then condense in separate reactions. This means that during calcination above 230 ° C under these conditions, the principal product is manganese–magnesium cyclo-tetraphosphate c-$MnMgP_4O_{12}$, formed by this reaction, although additional by-products—higher polyphosphoric acids—and intermediate products of the hydrogenphosphate type (e.g. $Mn_2P_2O_7$ and $Mg_2P_2O_7$) are also gradually formed. A part of the phosphoric component becomes volatile and, in addition to this there occurs a further drop in sample mass (above the value corresponding to the release of six water molecules from the starting dihydrogenphosphate) owing to the formation of ultraphosphates. Analysis of calcinates prepared at the same water vapour pressure (1 kPa) in an electric oven proved that c-$MnMgP_4O_{12}$ becomes the prevailing compound in the calcinate at temperatures above 330 ° C, making up more than 60% of the mixture of final products (at 600 ° C).

Open crucible and crucible with a lid

Thermogravimetric curves obtained using the open platinum crucible (Fig. 3, curve B: water vapour pressure about 5 kPa) and the crucible with a lid (Fig. 3, curve C: pressure about 20 kPa) resemble the two Q-TG curves (Fig. 3, curves A and D) described above. Curve B is very similar to curve A, while curve C is similar to curve D. This indicates that the mechanism of the dehydration and condensation reactions at vapour pressures of about 5 kPa is similar to that described for pressures approaching 1 kPa. The temperatures of the individual processes are simply shifted to higher values: for the release of water of crystallization the temperatures are higher by 2–15 ° C;

for molecules of constitutional water they are 5–20 °C higher. The share of the main product c-$MnMgP_4O_{12}$ in the sample is over 80% after TA has finished.

At vapour pressures of about 20 kPa (crucible with a lid) the reaction mechanism for the calcination of $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$ is similar to the mechanism described above for vapour pressures approaching 100 kPa. The temperatures of the individual processes are shifted to values lower by 0–50 °C. The share of the main product in the sample approaches 90% after TA has finished.

CONCLUSIONS

The series of reactions that takes place on the calcination of starting $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$ under water vapour pressures approaching 100 kPa is described by

$$Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$$

$$\xrightarrow[-4H_2O]{120\text{–}190\,°C} Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \xrightarrow[-H_2O]{190\text{–}250\,°C} Mn_{0.5}Mg_{0.5}H_2P_2O_7$$

$$\xrightarrow[-H_2O]{250\text{–}400\,°C\ (330\,°C)} c\text{-}MnMgP_4O_{12}$$

(The figure in brackets for the formation of the final product is the temperature at which the main part of the process occurs.) Binary manganese–magnesium cyclo-tetraphosphate c-$MnMgP_4O_{12}$ can be prepared in this way with a yield of over 97% w/w [32]. This new compound can be used as a special inorganic pigment for high-temperature applications [33].

If the calcination of the starting dihydrogenphosphate is carried out at lower water vapour pressures, certain intermediate products (anhydride or dihydrogendiphosphate) are partly split, to form hydrogenphosphates and phosphoric acid or diphosphates and diphosphoric acid, respectively, and single manganese and magnesium intermediates (i.e. not of binary type). These last then dehydrate and condense separately to by-products, thereby decreasing the share of the main product c-$MnMgP_4O_{12}$ in the final calcinate (up to 60%) at water vapour pressures approaching 1 kPa. The temperatures at which the principal parts of the individual reactions occur are also decreased.

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