

MECHANISM OF DEHYDRATION OF $Zn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 2H_2O$

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ABSTRACT

Thermal analyses under non-isothermal and under quasi-isothermal–isobaric conditions were used to follow the condensation reactions proceeding during the calcination of $Zn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 2H_2O$. Calcination in an electric oven under isothermal conditions was adopted for preparation of the intermediates and the main product, which were analysed by chromatography, IR spectroscopy, NMR spectroscopy, X-ray analysis, electron microscopy, and extraction experiments with solutions of water, acetone and 0.3 M HCl. The effect of water vapour pressure on the course of calcination has been monitored, in terms of the rate and yield of the condensation reactions and the formation of the main product and other products such as the new compound binary cyclotetraphosphate (tetrametaphosphate) $ZnMgP_4O_{12}$.

INTRODUCTION

The condensed phosphates of divalent metals are relatively stable compounds, both thermally and chemically [1,2]. They exhibit properties of colour [3,4], anticorrosion ability [5,6] and luminescence [7,8] which allow their application as special inorganic pigments [9]. In addition, they dissolve very slowly, which favours their application as slow-acting trace-element fertilizers [10]. Cyclotetraphosphates are formed by calcination of the dihydrogen phosphates of the respective metals, or of mixtures of phosphoric acid with the oxide, hydroxide or carbonate, with the $M^{II}O/P_2O_5$ molar ratio equal to unity [1,6]. Their synthesis has been studied by means of thermal analysis, especially under quasi-isothermal, quasi-isobaric conditions (Q-TA). Recently we have focused our attention on preparations of binary cyclotetraphosphates, i.e. those in which one part of the bivalent metal ion is replaced by the cheaper ion of an alkaline-earth metal (Ca or Mg) [11]. Such products have a lower price and their special properties are better [12]. These products have not been reported in the literature (see monographs 13–15). Our latest work shows that binary cyclotetraphosphates containing Mg exist [16,17]; their general formula is $M_{2-x}^{II}Mg_xP_4O_{12}$, where $0 < x < 2$.

EXPERIMENTAL

Pure $\text{Zn}_{0.5}\text{Mg}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ in the form of colourless crystals was prepared by the reaction of an aqueous suspension of zinc carbonate hydroxide and magnesium hydroxide carbonate with phosphoric acid at 60° for 5 h. The quality of the starting product was confirmed by X-ray diffraction analysis, and its morphology by electron microscopy.

For separation of the individual processes taking place during the calcination, the starting dihydrogenphosphate was submitted to simultaneous thermogravimetry (TG), differential TG and differential thermal analyses (DTA) under non-isobaric conditions (Fig. 1) by means of the latest type of derivatograph fitted with a microcomputer [18] (Derivatograph-C, produced by the Hungarian Optical Works (MOM), Budapest). (Pt crucible with lid, temperature increase 2°C min^{-1}).

In order to separate better the individual processes taking place during the calcination, and to follow the effect of water vapour on their course, we submitted the starting dihydrogenphosphate to thermal analysis (TA) under quasi-isothermal, quasi-isobaric conditions with the Derivatograph Q-1500 apparatus (MOM). The decomposition rate chosen was 0.4 mg min^{-1} (calculated for a 200 mg total weight change). Various types of platinum crucible (Fig. 2) were used for the measurements [19]: a multi-plate sample

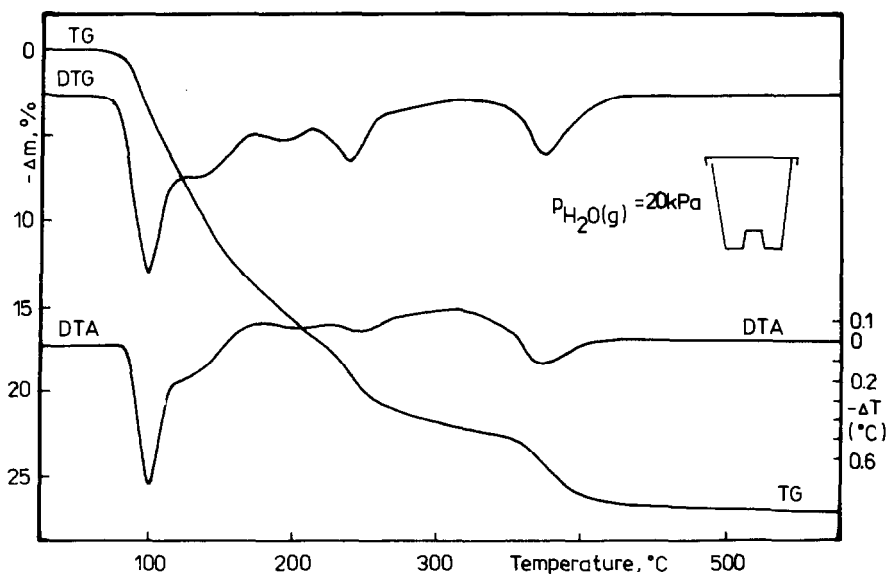


Fig. 1. Simultaneous TG, DTG and DTA curves of $\text{Zn}_{0.5}\text{Mg}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ under dynamic (non-isothermal) conditions. Apparatus, Derivatograph C; temperature, 2°C min^{-1} ; sample weight, 18.45 mg; standard, $\alpha\text{-Al}_2\text{O}_3$; sensitivity of TG balance 10 mg, of DTG balance 0.5, and of DTA balance 0.5; crucible with a lid, $p_{\text{H}_2\text{O}(\text{g})} = 20\text{ kPa}$; atmosphere, air.

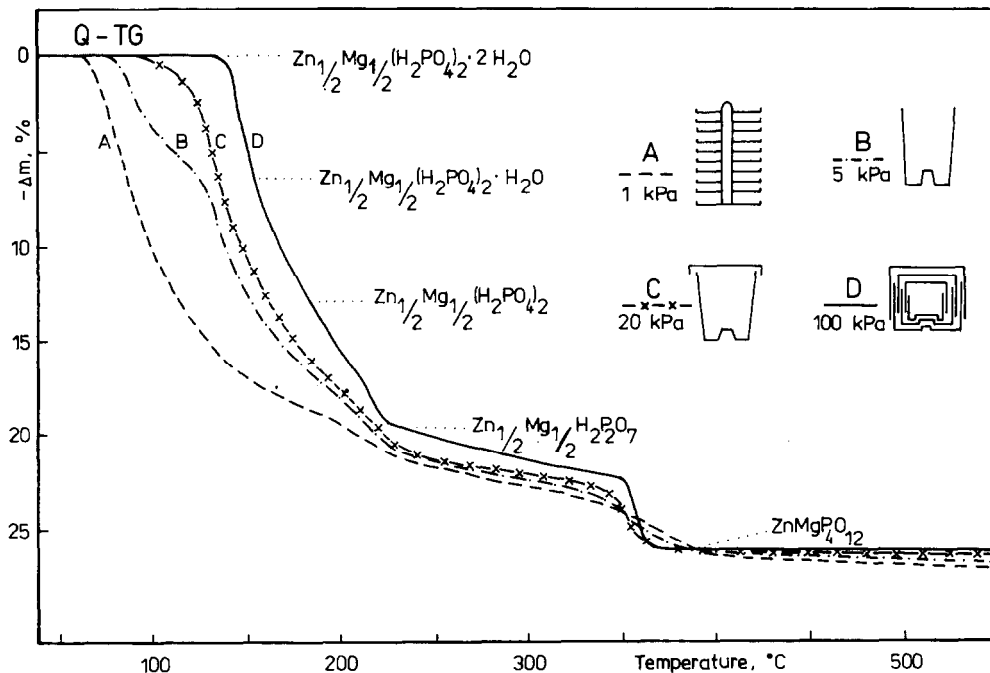


Fig. 2. Thermogravimetric curves of $Zn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 2H_2O$ under quasi-isothermal, quasi-isobaric conditions. Apparatus, Derivatograph Q-1500; decomposition rate 0.4 min^{-1} ; sample weight, 600 mg; atmosphere, air. A, Multi-plate crucible, $p_{H_2O(g)} = 1 \text{ kPa}$; B, open crucible, $p_{H_2O(g)} = 5 \text{ kPa}$; C, crucible with a lid, $p_{H_2O(g)} = 20 \text{ kPa}$; D, labyrinth crucible, $p_{H_2O(g)} = 100 \text{ kPa}$.

holder (curve A), an open crucible (curve B), a crucible with a lid (curve C) and a labyrinth crucible (curve D). These types of crucible retain the water vapour released during calcination of the starting material, the vapour pressure being 100 kPa (D), 20 kPa (C), 5 kPa (B) and 1 kPa (A) [19].

The conditions determined from the TA results were then adopted for preparation of the main condensation product and intermediates, i.e. by calcination of the starting dihydrogenphosphates in an electric oven with a controlled temperature increase of $2^\circ \text{C min}^{-1}$ at various temperatures; each sample was heated for 30 min under isothermal and isobaric conditions [$p_{H_2O(g)} = 100$ or 1 kPa].

The calcined materials were extracted with acetone (to separate the extractable phosphorus component, in the form of phosphoric acid or diphosphoric acid, from the dihydrogendiphosphate formed), with water (which dissolves the starting substance and the intermediate $MH_2P_2O_7$) or with 0.3 M HCl (to permit determination of the tetrametaphosphate content in the calcinate) [20].

Analyses of the individual samples prepared and identification of the products obtained from thermal analysis and calcination were carried out by

means of thin-layer chromatography [21], IR spectroscopy [22] (Perkin-Elmer 684 IR spectrophotometer), X-ray diffraction analysis [23,24] (HZG-4, G.D.R.), and electron microscopy (BS-300, Tesla, Czechoslovakia).

RESULTS AND DISCUSSION

Thermal analysis under non-isothermal (dynamic) conditions

From the thermoanalytical curves of the starting zinc(II)-magnesium(II) dihydrogenphosphate dihydrate, i.e. the binary salt $\text{Zn}_{0.5}\text{Mg}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Fig. 1), recorded under dynamic conditions with use of the crucible with a lid, it is obvious that five endothermic processes take place in total. They are always connected with mass decreases, whose sum is equal to 26.5% of the original sample mass. This decrease agrees accurately with the release of all five water molecules (two water of crystallization and two constitutional water molecules) from the starting dihydrogenphosphate (theoretical value 26.2%). The first molecule of water of crystallization is released in the endothermic process within the temperature interval 90–115°C. This action is followed by the second, less significant endothermic one of the release of the second molecule of water of crystallization in the range from 115 to 160°C. The first molecule of constitutional water is released in parts, viz. the first part in the range from 160 to 205°C and the second part in the range from 225 to 260°C. Their release is accompanied by two negligible endothermic processes. The second molecule of constitutional water is released in the broad range from 260 to 450°C; however, under these conditions, a considerable portion of this water is released in the range from 320 to 400°C, accompanied by a significant endothermic effect on the DTA curve.

Thermal analysis under quasi-isothermal, quasi-isobaric conditions

Thermal analysis under such conditions by means of a Derivatograph Q-1500 instrument, using four different crucibles as sample carriers, provided a more exact idea of the course of individual processes in the calcination of the starting $\text{Zn}_{0.5}\text{Mg}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Fig. 2).

Labyrinth crucible

If the labyrinth crucible is used as a sample carrier (Fig. 2, curve D), at first the water of crystallization from the starting $\text{Zn}_{0.5}\text{Mg}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ is released in one stage. This can be observed in the temperature range from 140 to 185°C. At 185°C the calcination residue represents the anhydride of the binary dihydrogenphosphate, $\text{Zn}_{0.5}\text{Mg}_{0.5}(\text{H}_2\text{PO}_4)_2$. Its existence and binary character were confirmed by IMA methods. The

overall temperature interval of release of total water of crystallization from $\text{Zn}_{0.5}\text{Mg}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (140–185 °C) is shifted higher by 15–30 °C than the temperatures of release of water of crystallization (under the same conditions) from the corresponding simple dihydrogenphosphates $\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$: 115–170 °C [25] and $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$: 130–170 °C [26]. (In part this finding confirms that this dehydration phase is not connected with a splitting of the binary dihydrogen phosphate into the simple dihydrogenphosphates.)

The first molecule of constitutional water is released in the temperature interval 185–230 °C. At the same time the first condensation reaction takes place, which produces the intermediate binary dihydrogendiphosphate $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{H}_2\text{P}_2\text{O}_7$ (which was also confirmed by instrumental analytical methods (IMA). The temperature range of formation and the existence of this important intermediate were also confirmed experimentally: samples of calcinates from the starting $\text{Zn}_{0.5}\text{Mg}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (prepared under isothermal conditions in an electric furnace) were extracted with acetone (see Fig. 3a; the interval 185–340 °C). This temperature range lies roughly between the intervals (and partially overlaps them) of formation and existence of the simple dihydrogenphosphates $\text{ZnH}_2\text{P}_2\text{O}_7$ and $\text{MgH}_2\text{P}_2\text{O}_7$ determined by both Q-TA [25,26] and extraction experiments (Figs. 3b and 3c). (The intervals were 170–280 °C and 170–390 °C for $\text{ZnH}_2\text{P}_2\text{O}_7$ and $\text{MgH}_2\text{P}_2\text{O}_7$, respectively.) Comparison of the three temperature intervals given confirms, to a certain extent, that the first condensation product formed by the calcination of $\text{Zn}_{0.5}\text{Mg}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ really exists in the binary form $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{H}_2\text{P}_2\text{O}_7$ and not as a mixture of the simple products $\text{ZnH}_2\text{P}_2\text{O}_7$ and $\text{MgH}_2\text{P}_2\text{O}_7$. (This result was confirmed by IMA as well as by electron microscopy of both the calcination products and solid residues after the acetone extraction.)

The last process consists in the release of the second molecule of constitutional water to yield the second condensation reaction: formation of cyclotetraphosphate. In the labyrinth crucible this proceeds within the temperature interval 230–370 °C, more than half of this water being released practically isothermally at 350–360 °C. Above 360 °C the sample mass effectively changes no more, and the product is binary zinc(II)–magnesium(II) cyclotetraphosphate $\text{ZnMgP}_4\text{O}_{12}$ (which was confirmed by IMA). This product is a newly identified substance not yet described in the literature, and is protected by a Czech patent [27]. The crystal structure of this product was: monoclinic system, $C/2c$ group, with the structural parameters $a = 1.1770(5)$ nm, $b = 0.8296(4)$ nm, $c = 0.9906(4)$ nm, $\beta = 118.92(2)^\circ$, volume of elementary cell 0.8468 nm³, density 3.181 g cm⁻³ (ρ calculated) and 3.25 g cm⁻³ (ρ experimental). A comparison of temperature ranges of formation of the respective simple products (under the same conditions)— $\text{Zn}_2\text{P}_4\text{O}_{12}$ and $\text{Mg}_2\text{P}_4\text{O}_{12}$ —shows that they are distinctly different. The zinc(II) product is formed at lower temperatures (260–330 °C) [25], whereas its mag-

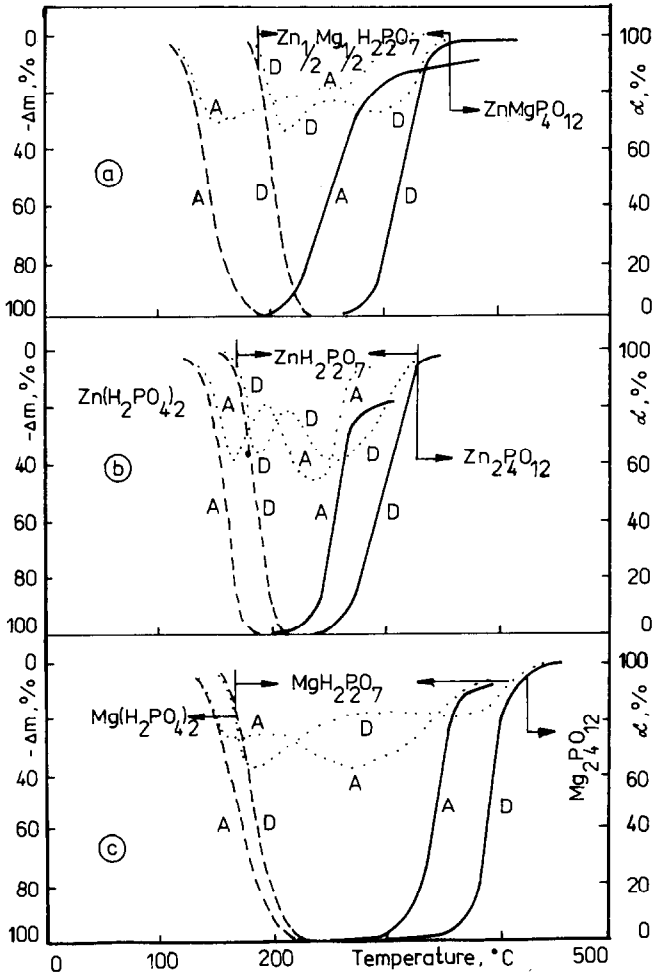


Fig. 3. Extraction experiments on calcinates of $\text{Zn}_{0.5}\text{Mg}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. Calcination conditions 2°C min^{-1} ; $p_{\text{H}_2\text{O}}(\text{g}) = 1\text{ kPa}$ (A) or 100 kPa (D). Weight changes determined by extraction: acetone ($\cdots\cdots$); water ($---$); 0.3 M HCl ($---$) (degree of conversion (α) to the cyclotetraphosphates).

nesium(II) counterpart is formed at higher temperatures ($390\text{--}460^\circ\text{C}$) [26]. These conclusions were confirmed by extraction experiments on the calcinates prepared under the respective conditions in an electric furnace; 0.3 M HCl was used for the extraction (see Fig. 3). At a water vapour pressure of about 100 kPa , calcinations of the individual dihydrogen phosphates $\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, and $\text{Zn}_{0.5}\text{Mg}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ produce the first portions of the final cyclotetraphosphates above the temperatures of 260 , 350 and 290°C , respectively. The final steady-state degree of conversion found in the individual calcinates under these conditions was 97% $\text{Zn}_2\text{P}_4\text{O}_{12}$ (at 350°C), almost 98% $\text{ZnMgP}_4\text{O}_{12}$ (at 360°C) and almost 99% $\text{Mg}_2\text{P}_4\text{O}_{12}$ (at 460°C).

Multi-plate crucible

The thermal analysis of $\text{Zn}_{0.5}\text{Mg}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ under quasi-isothermal–isobaric conditions using the multi-plate crucible, i.e. at a negligible water vapour pressure of 1 kPa in the area of the thermoanalysed sample, is represented by curve A in Fig. 2. The course of curve A is comparable with that of the above-described curve D (obtained with the labyrinth crucible).

In a comparison with the labyrinth crucible, the temperatures of the first two processes, i.e. the release of water of crystallization and the first constitutional water molecule, are shifted to values 30–80 °C lower. From the beginning of the release of the first portions of water of crystallization (65 °C) to the temperature rise of dihydrogendiphosphate (200 °C), no break is apparent on the Q-TG curve; i.e. dehydration takes place as though in one action. However, the course of the part of the Q-TG curve which is caused by the release of the second constitutional water molecule is rather variable. This is because, under these conditions at a low pressure of water vapour, the splitting of the intermediate ($\text{Zn}_{0.5}\text{Mg}_{0.5}\text{H}_2\text{P}_2\text{O}_7$) takes place to form zinc ($\text{ZnH}_2\text{P}_2\text{O}_7$) and magnesium ($\text{MgH}_2\text{P}_2\text{O}_7$) parts. These three intermediates then condense independently, and a mixture of cyclotetraphosphates ($\text{ZnMgP}_4\text{O}_{12}$, $\text{Zn}_2\text{P}_4\text{O}_{12}$, and $\text{Mg}_2\text{P}_4\text{O}_{12}$) arises. The temperature at which release of the last molecule of constitutional water ends is shifted to a value of approximately 400 °C (when formation of $\text{Mg}_2\text{P}_4\text{O}_{12}$ is complete [26]). Another difference consists in a continuous mass decrease of the thermoanalysed sample even after the mass decrease corresponding to the release of five water of crystallization molecules (theoretically 26.2%) has been attained: up to the final temperature of Q-TA at 580 °C, this additional mass decrease is 1%. At low water vapour pressures, part of the phosphorus component is split off from the individual intermediates and products and is condensed in independent reactions. The decrease in sample mass exceeding the value corresponding to the release of five water molecules from the starting dihydrogenphosphate is due to partial volatility of the phosphoric component and to the formation of ultraphosphates.

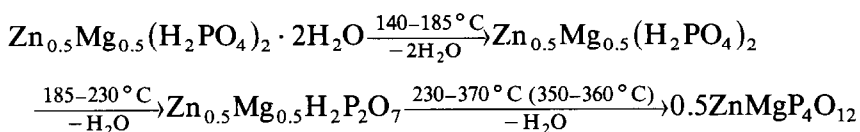
Open crucible and lid-covered crucible

The thermogravimetric curves obtained with application of the open platinum crucible (water vapour pressure 5 kPa, Fig. 2, curve B) and the lid-covered crucible (water vapour pressure ca. 20 kPa; Fig. 2, curve C) have shapes similar to those of the other two Q-TG curves (A and D in Fig. 3) discussed above. Curve B is closer to curve A, whereas curve C is closer to curve D. It is interesting to note that, in the case of the open crucible, the separation of the first molecule of water of crystallization clearly is distinct as a separate action (in the interval 80–125 °C). The possibility of splitting of the intermediate ($\text{Zn}_{0.5}\text{Mg}_{0.5}\text{H}_2\text{P}_2\text{O}_7$) is decreased with increasing vapour pressure. A portion of the main binary product ($\text{ZnMgP}_4\text{O}_{12}$) arises in the final calcination residues. At the same time, after the liberation of four water

molecules from the starting $\text{Zn}_{0.5}\text{Mg}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, a further decrease of the sample mass is less significant (i.e. above 370 or 380 °C).

CONCLUSION

The course and conditions of the reactions taking place during the calcination of $\text{Zn}_{0.5}\text{Mg}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ at a water vapour pressure close to 100 kPa in the sample area are expressed by the following scheme. (The temperatures corresponding to the course of the decisive part of the action are shown in brackets.)



In the way described in ref. 28 it is possible to prepare the binary cyclotetraphosphate $\text{ZnMgP}_4\text{O}_{12}$ with a yield of almost 98% (w/w).

If the calcination of the starting dihydrogenphosphate is performed at lower water vapour pressures, the intermediate is the dihydrogendiphosphate. These substances are then dehydrated and condensed separately to give side products; the amount of the main product $\text{ZnMgP}_4\text{O}_{12}$ in the final residue is thus decreased. At the same time, the temperatures of most individual dehydration reactions are lowered.

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