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Thermal behavior of acid phosphate salts $Ca_2MH_7(PO_4)_4{\cdot}2H_2O$ ($M = K^+$, NH_4^+) and $CaK_3H(PO_4)_2$

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ABSTRACT

New knowledge about various aspects of little-known acid salts is of great scientific and practical importance in view of their potential application in different areas such as proton conductors. For the first time, the thermal behavior of three acid phosphate salts, dicalcium potassium heptahydrogen tetrakis(phosphate) dihydrate ($Ca_2KH_7(PO_4)_4{\cdot}2H_2O$), dicalcium ammonium heptahydrogen tetrakis(phosphate) dihydrate ($Ca_2(NH_4)H_7(PO_4)_4{\cdot}2H_2O$) and calcium tripotassium hydrogenbis(phosphate) ($CaK_3H(PO_4)_2$), has been investigated. By means of simultaneous thermogravimetry, differential thermal and mass spectrometry analyses (TG/DTA/MS) the schemes of their thermal decomposition have been proposed. The two isostructural compounds $Ca_2KH_7(PO_4)_4{\cdot}2H_2O$ and $Ca_2(NH_4)H_7(PO_4)_4{\cdot}2H_2O$ are stable up to 90 – 95 °C and then undergo multiple-steps thermal decomposition process owing to dehydration of the crystallization water and dehydration-condensation. The anhydrous salt $CaK_3H(PO_4)_2$ exhibits very high thermal stability up to 530 °C. The products of the thermal decomposition have been identified.

1. Introduction

Proton conductors based on solid polyanionic compounds are attractive materials with a great potential for use as electrolytes in low and intermediate temperature fuel cells [1–3]. The main representatives include two classes of compounds: (i) acid inorganic salts such as (di) hydrogen phosphate, sulfate and selenates ($MHXO_4$, $M_3H(XO_4)_2$, $MH_5(XO_4)_2$, where M = K, Cs, Rb, NH_4; X = P, S, Se) and (ii) hydrated compounds such as heteropoly compounds ($H_4SiW_{12}O_{40}{\cdot}28H_2O$, $H_3PW_{12}O_{40}{\cdot}nH_2O$, etc.) and variety of phosphate hydrates of tetravalent/trivalent/bivalent metals (such as $H_3OUO_2PO_4{\cdot}3H_2O$, Ce$(HPO_4)_2{\cdot}nH_2O$, γ-Zr$(HPO_4)_2{\cdot}nH_2O$, etc.) [1,2]. The high proton conductivity in the first type of compounds is mainly attributed to the unique proton disorder in hydrogen-bond networks (predominant Grotthuss mechanism with proton hopping being associated with structural reorientation of the anions) [2,4,5]. In the second class of compounds, water-mediated proton conduction is predominant and different mechanisms have been proposed: vehicle-type proton transport mechanism or participation of adsorbed water molecules in creating H-bonding networks with effective pathways for proton conduction or surface hydration or H-bond interaction of water molecules with the bridging oxygen of the porous framework [6–9].

The present paper is a continuation of our systematic investigations on little known acid phosphates/arsenates like $Mg_2KH(XO_4)_2{\cdot}15H_2O$ (X = P, As) in view of their potential proton conductivity [10–13]. Our studies on the conducting properties of $Mg_2KH(XO_4)_2{\cdot}15H_2O$ (X = P, As) give evidence for interesting electric behavior with sharp increase in the conductivity to about 10^{-4} S cm^{-1} between 45 – 70 °C without structural changes [13]. Two relaxation mechanisms, through grains and grain boundaries, have been supposed. Based on the analysis of the frequency response of *ac* conductivity data, Zouari et al. have found that compounds $Na_3Mg_{1-x}Ca_xH(PO_4)_2$ (x = 0, 0.05 and 0.2) exhibit a sharp increase in the conductivity to about $1.4.10^{-2}$ Ω^{-1} cm^{-1} at 653 K (just before the thermal decomposition) [14]. It has been supposed that the conduction properties of these compounds are probably due to H^+ hopping mechanism [14]. A promising proton conductivity of $\sim 2.4.10^{-5}$ S cm^{-1} has also been reported for compositions $Ba_{3-x}K_xH_x(PO_4)_2$ at 250 °C [15]. These data raised our interest and motivation to study other little known acid salts from different points of view.

This work is devoted to the synthesis and investigation of the thermal behavior of three acid phosphate salts: $Ca_2KH_7(PO_4)_4{\cdot}2H_2O$, $Ca_2(NH_4)$

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$H_7(PO_4)_4{\cdot}2H_2O$ and $CaK_3H(PO_4)_2$. Similarly to $Mg_2KH(XO_4)_2{\cdot}15H_2O$ (X = P, As), $Na_3Mg_{1-x}Ca_xH(PO_4)_2$ and $Ba_{3-x}K_xH_x(PO_4)_2$ [14–16], $CaK_3H(PO_4)_2$ is also characterized by the presence of symmetric dimer units $H(PO_4)_2$ in its crystal structure [17]. The $Ca_2KH_7(PO_4)_4{\cdot}2H_2O$ and $Ca_2(NH_4)H_7(PO_4)_4{\cdot}2H_2O$ salts are isomorphous and have very complex crystal structure that consists of corrugated sheets of $[CaH_2PO_4]^+$ and $[H_3(PO_4)_2]^{3-}$ and between the sheets $[NH_4]^+$ (or K^+) and H_2O molecules are situated. Hydrogen bonds and Ca···O contacts hold tight the sheets thus forming a three-dimensional network [18,19]. Since the first reports on the synthesis and crystal structure determination of these salts, no further information can be found in the literature. We believe that new knowledge about the thermal stability and transformations of these acid salts will be of great importance for the correct interpretation and deep understanding of their conductivity behavior which is temperature-dependent. Moreover, the obtained information would be helpful for the potential application of the salts in different fields.

2. Experimental

Polycrystalline sample of $CaK_3H(PO_4)_2$ was prepared following the method previously described [20]. For the synthesis of $Ca_2KH_7(PO_4)_4{\cdot}2H_2O$ and $Ca_2(NH_4)H_7(PO_4)_4{\cdot}2H_2O$ we have developed new procedures which differ with these reported in [21] and are carried out at room temperatures.

2.1. Synthesis of $Ca_2MH_7(PO_4)_4{\cdot}2H_2O$ ($M = NH_4^+, K^+$)

A solution containing 2 ml 85% of phosphoric acid diluted with 5 mL of deionized water was added in small volume portions into a previously prepared suspension from 320 mg calcium carbonate and 5 mL of deionized water. At continuous stirring at room temperature, firstly, formation of foam due to release of carbon dioxide was observed, and after that the solution became clear. Then, another solution containing 400 mg of $(NH_4)_2HPO_4$ in 5 mL of deionized water was added. The resulting solution remained completely clear. To precipitate the product $Ca_2(NH_4)H_7(PO_4)_4{\cdot}2H_2O$, 15 mL of acetone was added in five portions of 3 mL each while continuously stirring the solution. The precipitate was then filtrated, rinsed twice with 2.5 mL of acetone and dried at ambient conditions.

Due to the close chemical composition and structure, the synthesis procedure for $Ca_2KH_7(PO_4)_4{\cdot}2H_2O$ is very similar to the one described above. The main difference here stands for the solution of $(NH_4)HPO_4$, which in this synthesis is replaced with a solution prepared by dissolving 560 mg $K_2HPO_4{\cdot}3H_2O$ in 4.8 mL of water. After all, the precipitation was the same initiated by the solvent exchange method using acetone in five portions of 3 mL each.

2.2. Synthesis of $CaK_3H(PO_4)_2$

28.6 g of K_2HPO_4 was introduced to a solution of 2.5 g KOH in 36 mL of deionized water. After all solid phase was dissolved (at continuous stirring) 30 mL 0.3 mol/dm^3 $Ca(CH_3COO)_2$ was added and the mixture was heated to 50 °C for 30 min. After filtration, the obtained crystals were rinsed with small amounts of water and acetone and dried at ambient conditions.

Hereafter, the following labeling of the salts will be used: C2KH7P for $Ca_2KH_7(PO_4)_4{\cdot}2H_2O$; C2NH7P for $Ca_2(NH_4)H_7(PO_4)_4{\cdot}2H_2O$ and CK3HP for $CaK_3H(PO_4)_2$.

The powder X-ray diffraction (XRD) patterns of the initial salts and of their thermal decomposition products were collected using Rigaku Ultima IV X-ray diffractometer (Tokio, Japan) and Bruker Advance 8 diffractometer (Karlsruhe, Germany), both operating with CuK_α radiation. For phase identification ICSD and ICDD databases have been used.

The thermal behavior of C2KH7P, C2NH7P and CK3HP was studied by means of simultaneous thermogravimetry and differential thermal analysis combined with mass spectrometry for gas analysis (TG/DTA/MS) using LABSYS^{TM} Evo apparatus (SETARAM, Caluireet-Cuire, France) equipped with a quadrupole mass spectrometer (Pfeiffer Vacuum, OmniStar GSD301, Switzerland). The thermal analysis was carried out in a platinum crucible by linear temperature increase up to 600 – 800 °C at a rate of 5 K min^{-1} in an argon flow, the samples mass being around 40 mg. Considering the chemical composition of the acid salts, the following selected gasses were analyzed: H_2O (m/z = 18), atomic oxygen (m/z = 16), molecular oxygen (O_2 with m/z = 32) and NH_3 (m/z = 17). The crystals were not grinded before TG/DTA/MS measurements in order to avoid a partial dehydration that could occur upon the grinding procedure. To get more insights about the chemical species formed after the thermal decomposition we have analyzed the XRD patterns of the samples obtained after annealing of the initial salts at 600 °C for 10 h in air media.

3. Results and discussion

The phase purity of the as-prepared acid salts was confirmed by their XRD patterns (Fig. 1). The observed diffraction peaks in the XRD patterns match very well with the standard patterns of the salts: ICSD-98–004–9694 for C2KH7P (Fig. 1a), ICSD-98–002–6019 for C2NH7P (Fig. 1b) and ICDD-01–076–1248 for CK3HP (Fig. 1c). For C2KH7P and C2NH7P only single crystal XRD data are available [18,19]. The obtained crystals of the three salts exhibit a preferred orientation which is related to their sheet-like structure [17–19]: along [010] direction for both C2KH7P and C2NH7P (Fig. 1a,b) and along [001] direction for CK3HP (Fig. 1c).

The TG/DTA/MS curves for the three salts are displayed in Figs. 2, 4 and 6.

3.1. $Ca_2KH_7(PO_4)_4{\cdot}2H_2O$ (C2KH7P)

The TG/DTA/MS data of C2KH7P show that it is stable up to 95 °C and then undergoes a thermal decomposition that is finished at 530 °C. The thermal decomposition process occurs in four steps supported by the four endothermic peaks with the maxima at 120.1 °C, 186.1 °C, 300.5 °C and 457.8 °C (Fig. 2), all of them being accompanied by the corresponding mass loss.

According to the experimental mass loss for the 1st step with T_{max} at 120.1 °C (Δm_{exp} = 6.30%) this step is related to the dehydration of the two crystallization water molecules (theoretical mass loss Δm_{th} = 6.64%) which leads to the formation of intermediate anhydrous salt with composition $Ca_2KH_7(PO_4)_4$ at 143 °C. There is no range of thermal stability of this anhydrous salt and it further undergoes series of dehydration - condensation processes, characteristic for acid salts where constitution water is removed [22–26]. This conclusion is fully supported by the MS data where signals for evolution of water are only detected (Fig. 2). Considering the formula $Ca_2KH_7(PO_4)_4$, an evolution of 7/2 mol of water can be expected at the end of the thermal decomposition. Based on mass loss calculation for the 2nd, 3rd and 4th step it can be supposed that 3/2 mol of water are evolved at the 2nd step (T_{max} at 186.1 °C), while the remaining 2 mol of water are gradually released over the temperature range 240 – 530 °C. In total, at the end of the thermal decomposition of C2KH7P, 11/2 mol of water are evolved in accordance with the very good agreement between the experimental and theoretical mass loss (Δm_{exp} = 18.03% *vs* Δm_{th} = 18.26%). Therefore, the following reactions take place:

(1) $Ca_2KH_7(PO_4)_4{\cdot}2H_2O \rightarrow Ca_2KH_7(PO_4)_4 + 2H_2O$ between 95 and 143 °C
(2) $Ca_2KH_7(PO_4)_4 \rightarrow$ "$Ca_2KH_4P_4O_{14.5}$" + $3/2H_2O$ between 143 and 240 °C
(3) "$Ca_2KH_4P_4O_{14.5}$" → "$Ca_2KP_4O_{12.5}$" + $2H_2O$ between 240 and 530 °C

It should be mentioned that the labels "$Ca_2KH_4P_4O_{14.5}$" and

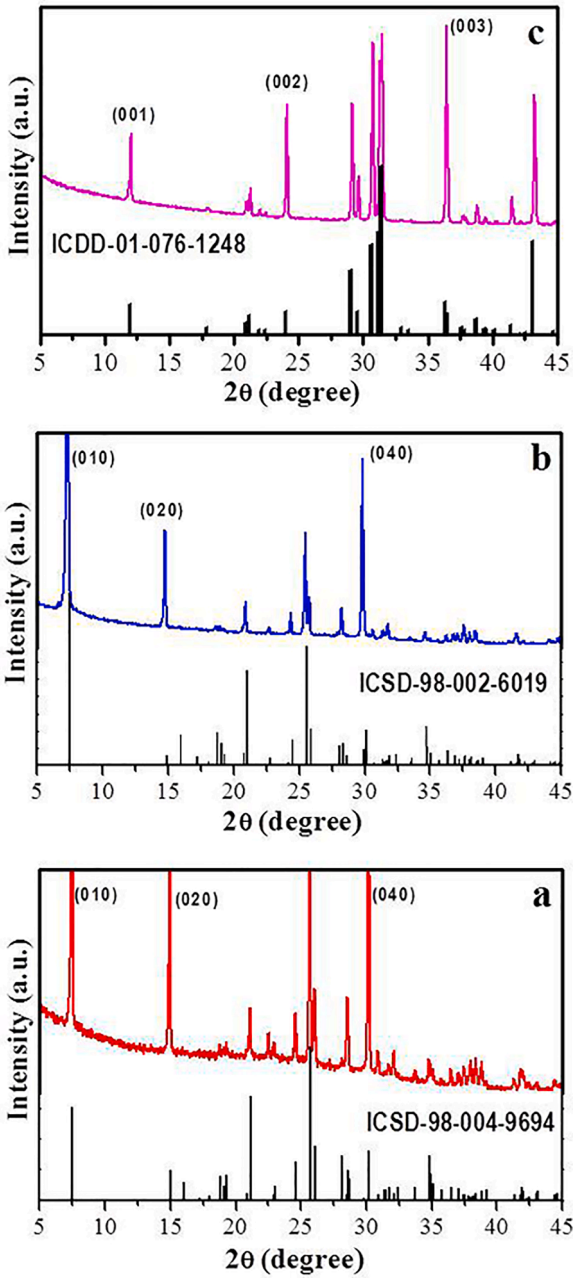

Fig. 1. XRD patterns of: (a) C2KH7P, (b) C2NH7P, (c) CK3HP.

"$Ca_2KP_4O_{12.5}$" in equations (2) and (3) are not true chemical formula for given compound. These labels reflect only the quantitative ratio of the chemical elements where the anion $P - O$ configuration cannot be predicted.

The products of the dehydration-condensation reactions of acid phosphate salts always consist of some condensed phosphates with a P : O ratio lower than 1 : 4, containing $P - O - P$ bonds in linear (polyphosphates) or cyclic linkage (cyclophosphates) [10,15,22-26]. So that, the formation of some condensed phosphates has to be expected since the P:O ratio in the final product of the thermal decomposition of C2KH7P is 1 : 3.125 (see equation (3)). The analysis of the XRD pattern of C2KH7P annealed at 600 °C (Fig. 3) reveals that a complex mixture containing at least three phases such as hexagonal $CaKP_3O_9$ (ICDD-01–072–3862), monoclinic $CaK_2P_2O_7$ (ICDD-01–072–3846) and orthorhombic $CaKP_3O_9$ (ICDD-00–029–0993) is formed, but there are unidentified peaks as well.

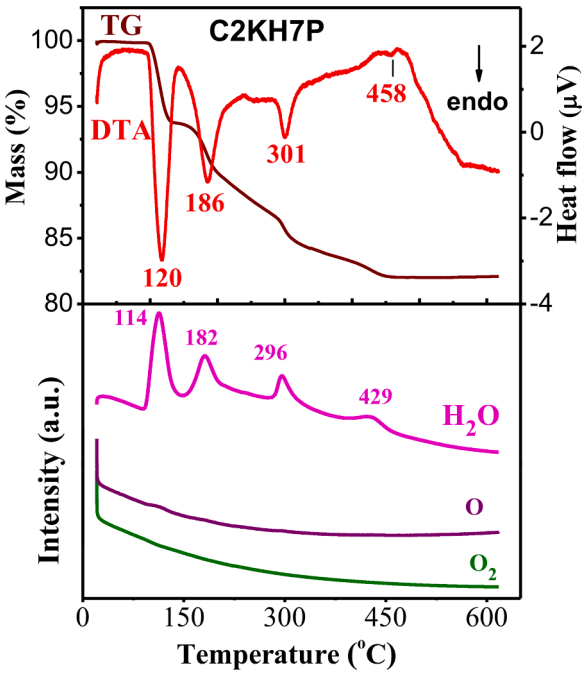

Fig. 2. TG/DTA/MS curves of $Ca_2KH_7(PO_4)_4{\cdot}2H_2O$.

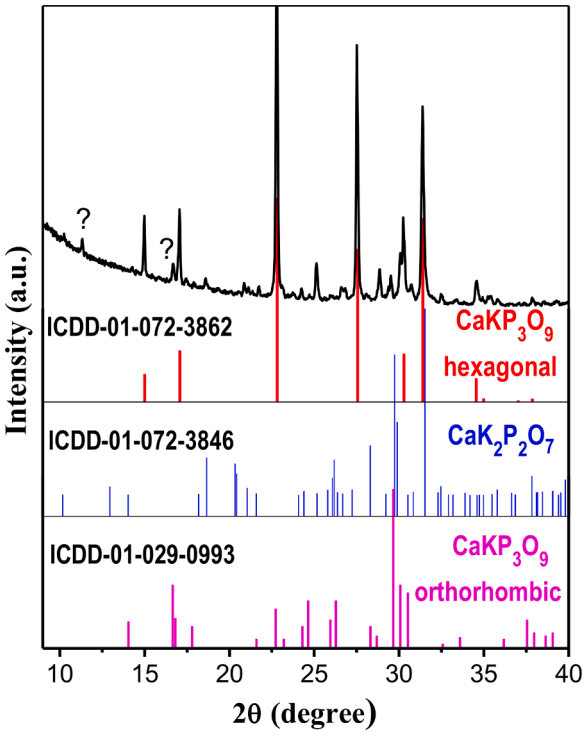

Fig. 3. XRD pattern of the products obtained after annealing of C2KH7P at 600 °C (?-unidentified peaks).

3.2. $Ca_2(NH_4)H_7(PO_4)_4{\cdot}2H_2O$ (C2NH7P)

The double salt C2NH7P containing ammonium undergoes a 5-step thermal decomposition process evident by the five endothermic DTA peaks (Fig. 4a) at temperature above 90 °C. In comparison with C2KH7P, here, there is one additional endothermic peak at 265 °C, whereas the remaining four DTA peaks appear at very close temperatures (Fig. 4b). This fact points to the similar thermal processes in the

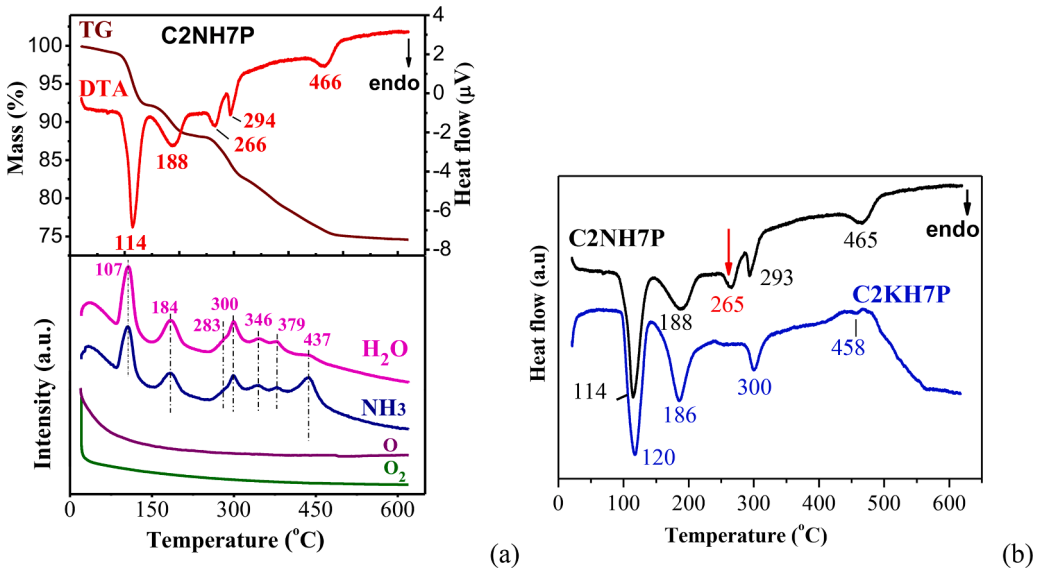

Fig. 4. (a) TG/DTA/MS curves of $Ca_2NH_4H_7(PO_4)_4{\cdot}2H_2O$; (b) Comparison of the DTA curves of C2KH7P and C2NH7P.

two salts, which can be expected because of their isostructurality.

The presence of NH_4^+ ions in the composition of C2NH7P premises a loss of ammonia in addition to the loss of water molecules. Unfortunately, our mass spectrometry equipment is not able to distinguish the very close *m/z* values differing by 1 amu as in the case of H_2O and NH_3 (*m/z* = 18 and *m/z* = 17, respectively). This limitation in the mass resolution is confirmed by our numerous experiments with different ammonium-containing phosphates (for instance $NH_4MPO_4.nH_2O$ $n = 1$ and 6). In the present study, as a prove for this statement, we have performed additional TG/DTA/Mass spectrometry experiment with potassium sample CaKH7P which does not contain any NH_4^+ ions in its composition, but a loss of NH_3 was also considered together with the loss of H_2O, atomic O and O_2 (Fig. S1). One can see from Fig. S1 that the profile and the positions of the signal for NH_3 are completely the same as these for H_2O, although the absence of NH_4^+. Because of that, it is not possible unequivocally to attribute the DTA peaks to the loss of H_2O and NH_3. Although, from the comparison of the DTA curves for C2NH7P and C2KH7P (Fig. 4b) it is reasonable to suppose that the peak at 265 °C could be related to the release of NH_3, while the remaining four peaks – to release of H_2O molecules. By analogy to the K-containing salt, the 1st step (T_{max} at 114.5 °C) can be attributed to the dehydration of the 2 mol crystallization water ($\Delta m_{exp} = 6.77\%$ *vs* $\Delta m_{th} = 6.91\%$), while the three other peaks at 188.1 °C, 293.5 °C and 465.8 °C – to the dehydration-condensation processes with release of 4 mol of constitution water. So that, the overall thermal decomposition process can be described with the following equation:

(4) $Ca_2(NH_4)H_7(PO_4)_4{\cdot}2H_2O \rightarrow 2Ca(PO_3)_2 + 6H_2O + NH_3$where Δm_{th} is 23.98% *vs* Δm_{exp}= 24.35%

The formation of calcium catena-phosphate, $Ca(PO_3)_2$ (ICDD-01–079–0700) at 600 °C as a final decomposition product of C2NH7P is confirmed by the XRD data (Fig. 5).

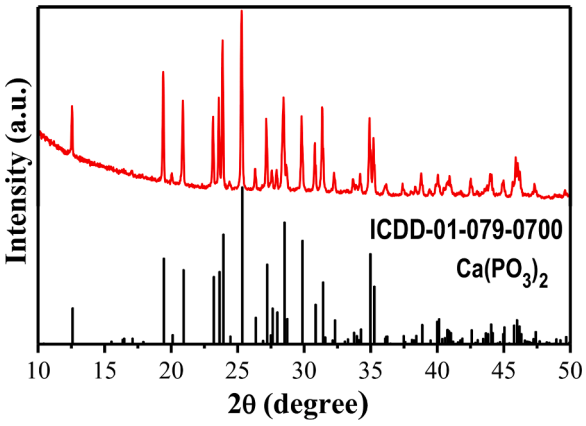

Fig. 5. XRD pattern of the product obtained after annealing of C2NH7P at 600 °C.

3.3. $CaK_3H(PO_4)_2$ (CK3HP)

The anhydrous salt $CaK_3H(PO_4)_2$ exhibits a very high thermal stability up to 530 °C (T_{onset}) when a dehydration-condensation process with release of a half water molecule takes place (Δm_{exp} = 2.27% *vs* Δm_{th} = 2.58%) (Fig. 6). This process is finished at 700 °C, the DTA peak being at 609.0 °C. There is no evidence from the DTA curve for any polymorphous phase transformations below 530 °C. Therefore, the following scheme of the thermal transformations can be proposed:

(5) $CaK_3H(PO_4)_2 \rightarrow$ "$CaK_3P_2O_7$" + 1/2H_2O between 530 and 700 °C

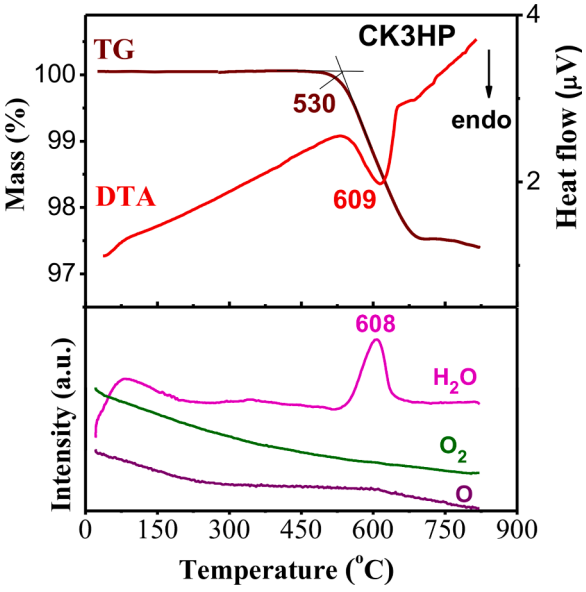

Fig. 6. TG/DTA/MS curves of $CaK_3H(PO_4)_2$.

Here, "$CaK_3P_2O_7$" is not given as a chemical compound but as a chemical composition of the final decomposition product that reflects only the molar ratio between the chemical elements.

Although the above very simple scheme, the thermal decomposition yields a complex mixture in which the presence of the hexagonal $KCaPO_4$ (ICDD-00–033–1002) as a main component is doubtless (Fig. 7). However, the identification of the remaining XRD peaks is ambiguous. Some possible phases are $CaK_2P_2O_7$ (ICDD-01–072–3846) and $KCa_{10}(PO_4)_7$ (ICDD-01–070–6159), but there is a discrepancy between the intensities of some of the peaks in the experimental and theoretical patterns (Fig. 7).

It should be mentioned that $CaK_3H(PO_4)_2$ shows considerably higher thermal stability in comparison with other closely-related compounds such as $Ba_{3-x}K_xH_x(PO_4)_2$ and $Na_3MgH(PO_4)_2$ and $Na_3Mg_{1-x}Ca_xH(PO_4)_2$. In the case of $Na_3MgH(PO_4)_2$ and Ca-containing compositions $Na_3Mg_{1-x}Ca_xH(PO_4)_2$ (x = 0, 0.05, 0.2) which are isostructural with $CaK_3H(PO_4)_2$, the loss of the constitution water occurs between 350 °C and 580 °C (T_{max} on DTA curves is around 540 °C) [14,27], while $Ba_{3-x}K_xH_x(PO_4)_2$ has even lower thermal stability with release of the water between 100 °C and 370 °C [15].

4. Conclusion

First data on the thermal behavior of three acid phosphate salts, $Ca_2KH_7(PO_4)_4{\cdot}2H_2O$, $Ca_2(NH_4)H_7(PO_4)_4{\cdot}2H_2O$ and $CaK_3H(PO_4)_2$, have been reported. By means of simultaneous thermogravimetric, differential thermal and mass spectrometry analyses, the schemes of their thermal decomposition have been established. The two isostructural compounds $Ca_2KH_7(PO_4)_4{\cdot}2H_2O$ and $Ca_2(NH_4)H_7(PO_4)_4{\cdot}2H_2O$ are stable up to 90 – 95 °C and then undergo multiple-steps thermal decomposition process up to 500 – 530 °C. The dehydration of the two crystallization waters occurs between 90 °C and 145 °C and this process is clearly distinguished from the several dehydration–condensation processes occurring between 150 °C and 500 – 530 °C. The salt $CaK_3H(PO_4)_2$ exhibits very high thermal stability up to 530 °C when 1/2 mole of constitution water is released. The products of the thermal decomposition consist of condensed phosphates or mixtures of condensed phosphates and orthophosphates. This new knowledge about the thermal stability and thermal transformations of $Ca_2KH_7(PO_4)_4{\cdot}2H_2O$, $Ca_2(NH_4)H_7(PO_4)_4{\cdot}2H_2O$ and $CaK_3H(PO_4)_2$ provides valuable data in view of their potential application in different areas.

Author.ßcontributions

V. Koleva: Conceptualization, Methodology, Interpretation of data, Figure preparation, Writing- Original draft, Reviewing and Editing. **K. Najkov:** Synthesis, Investigation, Formal analysis. **M. Najdoski:** Synthesis, Investigation, Resources. **V. Stefov:** Supervision, Writing-Reviewing and Editing.

Conflict of interest and authorship conformation form

Please check the following as appropriate:

X All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.

X This manuscript has not been submitted to, nor is under review at, another journal or other publishing venue.

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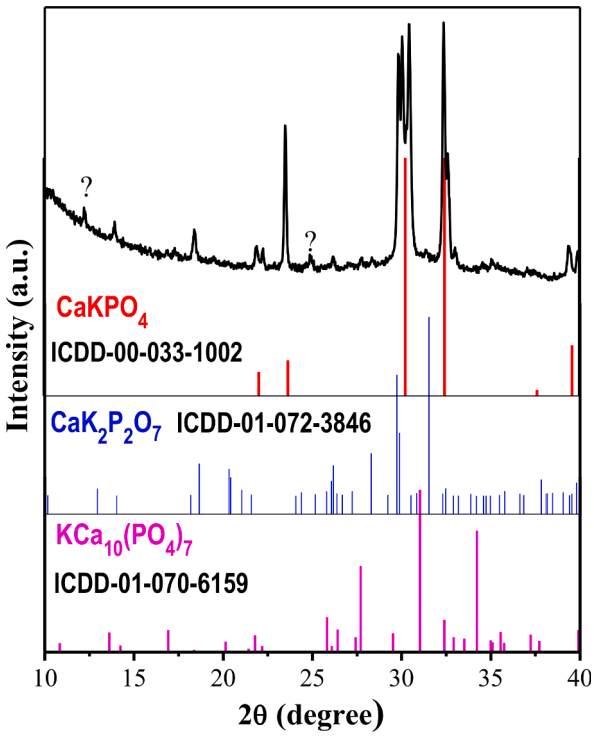

Fig. 7. XRD pattern of the products obtained after annealing of CK3HP at 600 °C (?-unidentified peaks).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.tca.2023.179518.

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