

New layered caesium zinc hydrogen phosphate, $\text{CsZn}_{2.5}(\text{HPO}_4)_3 \cdot 2\text{H}_2\text{O}$; synthesis, crystal structure and thermal transformation

Torben R. Jensen^{*†a} and Rita G. Hazell^b

^a Chemistry Department, University of Southern Denmark, Odense University, DK-5230 Odense M, Denmark

^b Chemistry Department, University of Aarhus, DK-8000 Aarhus C, Denmark

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The synthesis, crystal structure and thermal transformation of a new caesium zinc hydrogen phosphate hydrate, $\text{CsZn}_{2.5}(\text{HPO}_4)_3 \cdot 2\text{H}_2\text{O}$, is reported. This material crystallised from a gel with molar composition 1 ZnO :0.48 P_2O_5 :0.24 Cs_2O :12 H_2O :4.8 MeCO_2H , and pH of 1.0, after two months at room temperature. The crystal structure of $\text{CsZn}_{2.5}(\text{HPO}_4)_3 \cdot 2\text{H}_2\text{O}$ has layers built from PO_4 and ZnO_4 tetrahedra and with other zinc atoms forming octahedra by coordination to water molecules. The zinc octahedra are placed across pseudo 12-rings and caesium ions are placed above and below eight-ring openings. Thermal analysis was performed using thermogravimetric (TG) and differential scanning calorimetric (DSC) measurements. Two weight losses were detected and assigned to expulsion of crystal water and water from condensation of hydrogen phosphate. DSC was used to estimate enthalpy changes from three thermal events.

Introduction

Phosphate chemistry has received considerable interest during the past two decades owing to the large structural diversity found for those materials within a variety of different chemical compositions.¹ Different classes of porous materials have been investigated due to their adsorptive and ion exchange properties, e.g. layered and pillared phosphates and phosphonates, and also mesoporous materials.² The latter are exemplified by the zinc phosphates, $[\text{C}_n\text{H}_{2n+1}\text{NMe}_3\text{Br}]\cdot\text{ZnHPO}_4$ with $9 < n < 21$, which have layer distances in the range ca. 22–32 Å.³ A major discovery in the early 1980s was a new family of microporous aluminium phosphates (APO), and variants (MAPO) where metal ions substitute a part of the aluminium framework atoms, which have contributed to a steadily growing number of structure types in the zeolite nomenclature.⁴ APO and MAPO materials are usually templated by amine cations and especially the metals Mg, Co and Zn have provided new members to the MAPOs.⁵ Fully aluminium substituted phosphate materials, e.g. $\text{Al}^{3+} \rightarrow \text{Zn}^{2+} + \text{M}^+$ where M = alkali metal, might have increased thermal stability and thereby attract more attention to application of the important catalytic properties observed for MAPOs.⁶ Furthermore, during the 1990s other new groups of orthophosphate materials were discovered, often templated by amine cations, $\text{M}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot \text{amine} \cdot \text{H}_2\text{O}$.⁷ The metals can be Mg, Mn, Co or Zn or can have mixed valence like Fe(II)/Fe(III) and Ti(III)/Ti(IV).⁸ New members of this orthophosphate manifold of materials can possibly have future industrial applications similar to the well known zeolites A, X and Y, e.g. catalysis and adsorption.⁹

Materials with open structures are topologically metastable and are therefore prepared at moderate temperatures usually using solvothermal methods.¹⁰ It has been found that decreasing the synthesis temperature increases the nucleation time,¹¹ e.g. $\text{Rb}_2\text{Zn}_2(\text{HPO}_4)_3$ crystallised after 4.5 months at 52 °C.¹² Successive phase transformations can be observed upon pro-

longed thermal treatment where the phases formed have higher thermodynamic stability,¹³ e.g. $\beta\text{-LiZnPO}_4 \cdot \text{H}_2\text{O}$, prepared by solution mediated conversion of $\alpha\text{-LiZnPO}_4 \cdot \text{H}_2\text{O}$, a phase with 2.5% lower density.¹⁴ We have also discovered a templated zinc phosphate, $\text{LiZn}(\text{HPO}_4)(\text{PO}_4) \cdot \text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3 \cdot \text{H}_2\text{O}$, which crystallised after ca. 3 months at room temperature by solvothermal conversion of a microporous material, $\text{Zn}_2(\text{PO}_4)_2 \cdot \text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3$, DAF-3.¹⁵ Remarkably, hydrothermal synthesis in nature has led to an iron phosphate mineral, cacoxenite, with channels of ca. 14 Å, despite the general topological metastability of microporous materials.¹⁶ Laboratory hydrothermal synthesis has recently produced other fascinating materials, e.g. a zinc phosphate with pores formed by 24 tetrahedra and with a free diameter of 10.5–14.8 Å.¹⁷

We present the synthesis method, crystal structure and thermal decomposition of a new layered caesium zinc hydrogen phosphate hydrate, $\text{CsZn}_{2.5}(\text{HPO}_4)_3 \cdot 2\text{H}_2\text{O}$.

Experimental

Hydrothermal synthesis

The system, $\text{Cs}_2\text{O}-\text{ZnO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$, was explored using solvothermal synthesis and a relatively high amount of acetic acid. A thick white gel was prepared adding H_2O (13 mL) and MeCO_2H (15 mL) to powdered CsCl (3.477 g) and $\text{Zn}(\text{MeCO}_2)_2 \cdot 2\text{H}_2\text{O}$ (20.257 g). To this mixture 50% aqueous CsOH (4.720 g) and then 85% H_3PO_4 (10.134 g) were added slowly under stirring. The molar composition of the gel was 1 ZnO :0.48 P_2O_5 :0.24 Cs_2O :12 H_2O :4.8 MeCO_2H ; the chloride content relative to the amount of zinc was 0.31, and the pH of the gel was 1.0. This batch was divided into four portions denoted A, B, C and D. A portion of the gel, A, was placed in a Teflon lined steel autoclave and heated to 150 °C for 5 days. Portions B, C and D, were placed in sealed Pyrex flasks to prevent evaporation of the solvent and allowed to stand at 52 °C for 6 months, at room temperature for 2 months and at 5 °C for 8 months, respectively. The products were washed with water and ethanol and then dried in air. The synthesis was performed using the following commercial chemicals: CsCl (Merck, suprapur,

† Present address: Condensed Matter Physics and Chemistry Department, Risø National Laboratory, DK-4000 Roskilde, Denmark. E-mail: torben.rene.jensen@risoe.dk

>99%), 50% CsOH (Aldrich, 99%), 85% H₃PO₄ (Fluka, extra pure, >98%), Zn(MeCO₂)₂·2H₂O (Fluka, *purum* p.a. >99.0%) and MeCO₂H (pure, >99%).

Powder diffraction

Initial phase identification was performed using X-ray diffraction on single-crystal and powder samples. Powder diffraction data for phase identification and refinement of unit cell parameters were obtained using a Siemens D5000 diffractometer equipped with a primary germanium monochromator (Cu-K α ₁ radiation, $\lambda = 1.54060$ Å). The data was collected in the 2θ range 5–90 with a step length of 0.02° and counting time of 2–15 s per step. The program CELLKANT was used to refine the unit cell parameters from the observed d spacings.¹⁸

Single crystal diffraction

A clear, colourless crystal fragment of CsZn_{2.5}(HPO₄)₃·2H₂O (0.10 × 0.10 × 0.03 mm) was used for the data collection performed on a Siemens SMART diffractometer equipped with a CCD detector and graphite monochromated Mo-K α radiation, $\lambda = 0.71073$ Å, using the SMART program.¹⁹ Data were corrected for Lorentz–polarisation effects and for absorption using an empirical method (program SADABS).¹⁹

A structural model was found in space group $P\bar{1}$ (no. 2) using direct methods as implemented in the program SIR97.²⁰ Programs from the KRYSTAL software package were used for structure refinement.²¹ Hydrogen atoms were placed one third of the distance between the oxygens and refined isotropically. All other atoms were refined with anisotropic displacement parameters. The program Atoms Ver. 4.0 was used for preparation of the polyhedra drawings of the crystal structure.²²

Crystal data. CsZn_{2.5}(HPO₄)₃·2H₂O, $M = 620.34$, triclinic, space group $P\bar{1}$ (no. 2) $a = 8.3918(6)$, $b = 9.8254(8)$, $c = 9.9090(7)$ Å, $\alpha = 111.172(1)$, $\beta = 111.751(1)$, $\gamma = 97.560(1)^\circ$, $U = 673.59$ Å³, $T = 120$ K, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 7.52$ mm⁻¹, 17148 reflections measured, 2340 unique reflections ($R_{\text{int}} = 0.021$) which were used in all calculations. The final $wR(F^2) = 0.061$ and $R1 = 0.032$.

CCDC reference number 186/2078.

See <http://www.rsc.org/suppdata/dt/b0/b000714p/> for crystallographic files in .cif format.

Thermal investigation

A thermogravimetric measurement (TG) was performed between 30 and 500 °C, using a SETARAM TG 92-12 instrument, nitrogen atmosphere and a heating rate of 5 °C min⁻¹. The sample was kept in an open Al₂O₃ crucible. Differential scanning calorimetric (DSC) measurements between 20 and 700 °C with a heating rate of 5 °C min⁻¹ were performed using a SETARAM 92-16.18 instrument, argon atmosphere and open platinum crucibles for the sample and the reference, Al₂O₃. The temperature and enthalpy change calibration of the DSC measurement was performed using the low to high quartz transition.

Results and discussion

Synthesis

Needle shaped crystals of triclinic CsZn₃(HPO₄)₂PO₄ (*ca.* 95%) and polyhedra of an orthorhombic caesium zinc chloride, Cs₂ZnCl₄, were obtained from portion A (heated to 150 °C for 5 days).²³ A small amount of thin needle shaped crystals of CsZn₃(HPO₄)₂PO₄ along with semi-amorphous material were recovered from portion B (52 °C, 6 months).^{23a}

Crystallisation of the new layered caesium zinc hydrogen-phosphate, CsZn_{2.5}(HPO₄)₃·2H₂O discovered in this work was noticed after 2 months at room temperature (portion C) [tri-

clinic, $a = 8.388(1)$, $b = 9.830(2)$, $c = 9.907(1)$ Å, $\alpha = 111.21(1)$, $\beta = 111.70(1)$ and $\gamma = 97.56(1)^\circ$, $U = 673.5(2)$ Å³, based on 74 reflections measured by powder diffraction]. This new material will be discussed in the following. A white unidentified semi-amorphous precipitate was recovered from portion D (placed at 5 °C for 8 months).

There is no direct relation between the starting composition of the gel and the chemical formula of the product for a hydrothermal synthesis. Physical and chemical conditions as temperature and time and the composition of the gel determine which phases nucleate in the gel acting as centres for crystal growths.¹⁰ This is exemplified above where several phases were prepared from the same reaction mixture. The new material CsZn_{2.5}(HPO₄)₃·2H₂O formed after a nucleation period of two months. The phase stability field of CsZn_{2.5}(HPO₄)₃·2H₂O is in a narrow temperature range ($5 < T < 52$ °C) and other synthesis experiments suggest that it only exists in a limited range of initial compositions of the gel. This investigation shows that the moderate temperature range can be important for solvothermal synthesis of new phosphate materials where the nucleation and crystal growth are slow processes. Successive phase transformations can in some cases be utilised for preparation of novel phase pure products by removing the solvent at the right moment and thereby stopping the reaction, *i.e.* kinetic control.¹³ In this case, the amount of solvent used is low and the species in the gel (*e.g.* clusters of ions or complexes) that form the initial nuclei are unknown. It has been proposed for the synthesis of some aluminium phosphate materials that initially chain-like structures are formed. Prolonged heating or increased temperature can transform chain-like structures to other more dense phases, *i.e.* layered phases or 3D frameworks.²⁴

Crystal structure of CsZn_{2.5}(HPO₄)₃·2H₂O

The crystal structure of CsZn_{2.5}(HPO₄)₃·2H₂O is built from regular tetrahedra of PO₄ and ZnO₄ and with other zinc atoms placed on inversion centres and coordinated to four water oxygens forming octahedra. Selected bond lengths and angles are listed in Table 1, which shows that each of the phosphate tetrahedra have one longer P–O bond revealing hydrogen on O(4), O(8) and O(12). Chains of alternating Zn(1,2)O₄ and P(1,3)O₄ tetrahedra are connected in pairs forming 4-ring ladders, which propagate in the c direction. In the zeolite terminology this is a crank shaft shaped 4-ring chain as visualised in Fig. 1.²⁵ These 4-ring chains are connected by P(2)O₄ tetrahedra to form a layer illustrated in Fig. 1 as a b,c projection of the crystal structure of CsZn_{2.5}(HPO₄)₃·2H₂O. The Zn(3) atoms are placed across pseudo 12-ring openings and coordinate to water oxygens. An a,b -projection of one layer is shown in Fig. 2 revealing 8-ring openings with caesium placed above and below. The crystal structure of CsZn_{2.5}(HPO₄)₃·2H₂O is built by stacking layers in the a -direction, which are held together by hydrogen bonding and Cs–O bonds. Fig. 3 shows the interconnection of layers stacked with the sequence, AAA.

Oxidation states, V_i , were calculated using the bond lengths shown in Table 1 not including the H atoms and the results are given in Table 2.²⁶ Framework oxygen atoms (no. 2, 6, 7 and 11) coordinated to one Cs, Zn and P each have V_i in the range 1.96–2.03, in agreement with the expected (numerical) value, 2.0. The sum of V_i for the ten oxygens participating in hydrogen bonding as donor or acceptor is 13.11 [O(8) acts both as donor and acceptor]. This is in accordance with the missing bond valence from seven H atoms. The cations P and Zn have calculated oxidation states in agreement with the expected values of 5 and 2, respectively. Caesium has $V_i = 0.78$ which is lower than the expected oxidation state because of a relatively low number of oxygen contacts, seven, in the first coordination sphere. The calculated bond valence for Cs is, $V_i = 0.89$, also including oxygen contacts in the range 3.59–3.68 Å to O(4), O(5) and

Table 1 Selected bond lengths (Å) and angles (°) for the crystal structure of CsZn_{2.5}(HPO₄)₃·2H₂O

| | | | | | | | |
|---------|----------|-------------|----------|----------|----------|------------|-----------|
| Zn1–O11 | 1.936(4) | O9–Zn1–O11 | 107.9(2) | P3–O9 | 1.500(4) | O9–P3–O11 | 114.1(2) |
| Zn1–O9 | 1.952(4) | O5–Zn1–O11 | 110.5(2) | P3–O11 | 1.508(4) | O9–P3–O10 | 108.2(2) |
| Zn1–O5 | 1.956(4) | O3–Zn1–O11 | 117.1(2) | P3–O10 | 1.538(4) | O9–P3–O12 | 109.9(2) |
| Zn1–O3 | 1.973(4) | O5–Zn1–O9 | 106.9(2) | P3–O12 | 1.586(4) | O10–P3–O11 | 112.6(2) |
| Mean | 1.954 | O3–Zn1–O9 | 108.1(2) | Mean | 1.533 | O11–P3–O12 | 102.8(2) |
| | | O3–Zn1–O5 | 105.9(2) | | | O10–P3–O12 | 109.1(2) |
| Zn2–O7 | 1.938(4) | O7–Zn2–O10 | 109.9(2) | Cs–O2 | 3.060(4) | O2–Cs–O7 | 91.0(1) |
| Zn2–O10 | 1.951(4) | O1–Zn2–O7 | 107.7(2) | Cs–O7 | 3.122(4) | O2–Cs–O6 | 83.3(1) |
| Zn2–O1 | 1.933(4) | O2–Zn2–O7 | 105.1(2) | Cs–O6 | 3.213(4) | O2–Cs–O14 | 121.8(1) |
| Zn2–O2 | 1.937(4) | O1–Zn2–O10 | 117.3(2) | Cs–O14 | 3.257(5) | O2–Cs–O11 | 128.0(1) |
| Mean | 1.940 | O2–Zn2–O10 | 112.3(2) | Cs–O11 | 3.346(4) | O2–Cs–O12 | 170.26(9) |
| | | O1–Zn2–O2 | 103.7(2) | Cs–O12 | 3.350(4) | O2–Cs–O8 | 82.5(1) |
| | | | | Cs–O8 | 3.407(4) | O6–Cs–O7 | 104.4(1) |
| Zn3–O6 | 1.990(4) | O6–Zn3–O13 | 86.6(2) | Mean | 3.251 | O6–Cs–O14 | 53.3(1) |
| Zn3–O13 | 2.146(5) | O6–Zn3–O14 | 92.6(2) | O4–H4 | 0.64(8) | O6–Cs–O11 | 58.0(1) |
| Zn3–O14 | 2.202(4) | O13–Zn3–O14 | 90.5(2) | O8–H8 | 0.99(7) | O6–Cs–O12 | 89.7(1) |
| Mean | 2.113 | | | O12–H12 | 1.11(8) | O6–Cs–O8 | 164.8(1) |
| P1–O2 | 1.516(4) | O1–P1–O2 | 113.4(2) | O13–H13a | 0.87(6) | O7–Cs–O14 | 132.1(1) |
| P1–O1 | 1.528(4) | O2–P1–O3 | 110.5(2) | O13–H13b | 1.17(12) | O7–Cs–O11 | 69.5(1) |
| P1–O3 | 1.540(4) | O2–P1–O4 | 104.2(2) | O14–H14a | 0.99(10) | O7–Cs–O12 | 84.2(1) |
| P1–O4 | 1.563(5) | O1–P1–O3 | 109.2(2) | O14–H14b | 0.79(9) | O7–Cs–O8 | 70.4(1) |
| Mean | 1.537 | O1–P1–O4 | 110.4(2) | | | O8–Cs–O11 | 128.97(9) |
| | | O3–P1–O4 | 108.9(2) | H8–O5 | 1.58(7) | O8–Cs–O12 | 103.6(1) |
| P2–O6 | 1.479(4) | O5–P2–O6 | 112.0(2) | H12–O10 | 1.60(8) | O8–Cs–O12 | 103.6(1) |
| P2–O5 | 1.535(4) | O6–P2–O7 | 113.8(2) | H14a–O8 | 1.80(10) | O8–Cs–O14 | 140.7(1) |
| P2–O7 | 1.517(4) | O6–P2–O8 | 106.5(2) | H13b–O1 | 1.91(12) | O11–Cs–O12 | 42.34(9) |
| P2–O8 | 1.585(4) | O5–P2–O7 | 107.6(2) | H13a–O9 | 1.97(7) | O11–Cs–O14 | 62.8(1) |
| Mean | 1.529 | O5–P2–O8 | 107.1(2) | H4–O3 | 2.06(8) | O12–Cs–O14 | 57.6(1) |
| | | O7–P2–O8 | 109.5(2) | | | | |

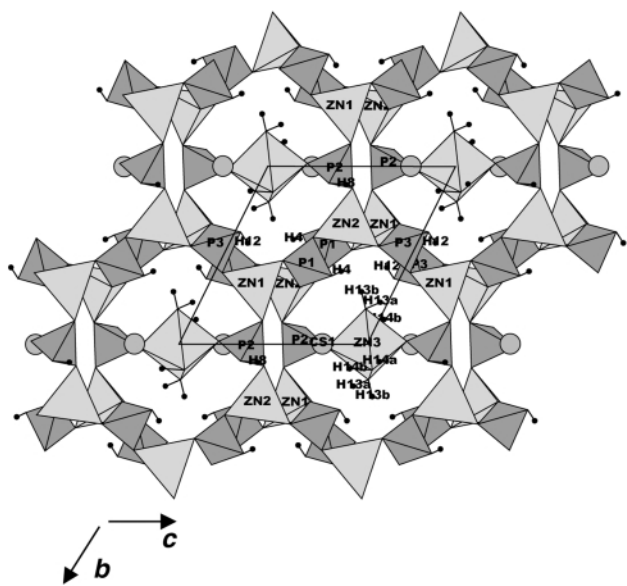


Fig. 1 The crystal structure of CsZn_{2.5}(HPO₄)₃·2H₂O shown as a *b,c*-projection; 4-ring chains of alternating Zn(1,2)O₄ and P(1,3)O₄ tetrahedra propagating in the *c* direction are connected by P(2)O₄. The Zn(3) octahedra are placed across pseudo 12-ring openings and coordinate to water oxygens. Tetrahedra of PO₄ are dark, ZnO₄ and ZnO₆ are grey, hydrogen atoms are shown as small black circles, Cs atoms as larger grey circles.

O(7)* [O(7)* is symmetry related to O(7)]. The relatively low calculated oxidation state for Cs might be due to the relatively open structure.

Thermal analysis

The weight loss as a function of temperature is shown in Fig. 4(a), and the measurement is in accordance with the formula CsZn_{2.5}(HPO₄)₃·2H₂O giving an observed weight loss of 9.4% between 90 and 430 °C (calculated mass loss 10.2%). A significant mass loss of 5.6% in the range 90–130 °C is

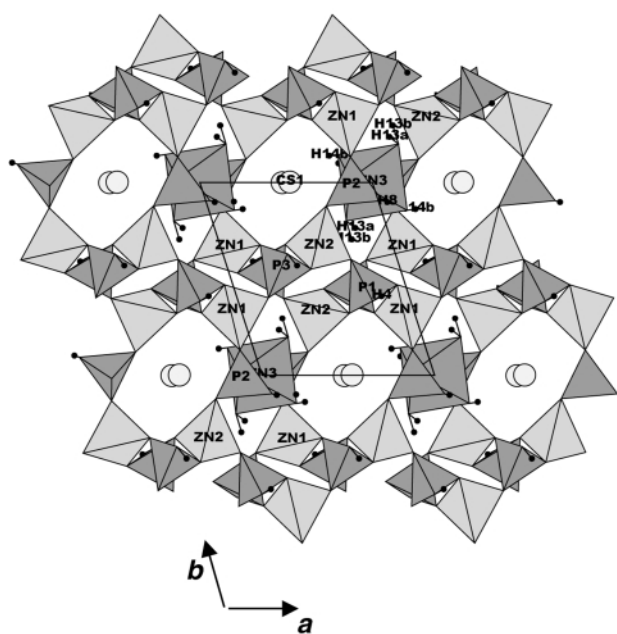


Fig. 2 An *a,b*-projection of the crystal structure of CsZn_{2.5}(HPO₄)₃·2H₂O reveal 8-ring openings with caesium placed above and below. Tetrahedra of PO₄ are dark, ZnO₄ and ZnO₆ are grey, hydrogen atoms are shown as small black circles, Cs atoms as larger grey circles.

observed, in accordance with loss of two molecules of crystal water per formula unit (calculated mass loss 5.8%). In the temperature range 180–430 °C a weight loss of 3.8% is observed, which might be due to condensation of hydrogen phosphate units and the expulsion of 1.5 H₂O per unit of CsZn_{2.5}(HPO₄)₃·2H₂O (theoretical mass loss 4.4%).

Differential scanning calorimetry of CsZn_{2.5}(HPO₄)₃·2H₂O revealed three thermal events on the heating curve as shown in Fig. 4(b). An endothermic event in the temperature range 88–143 °C with two peak values at 112 and 128 °C and a total enthalpy change $\Delta H = 157 \pm 42$ kJ mol⁻¹ is equivalent to the

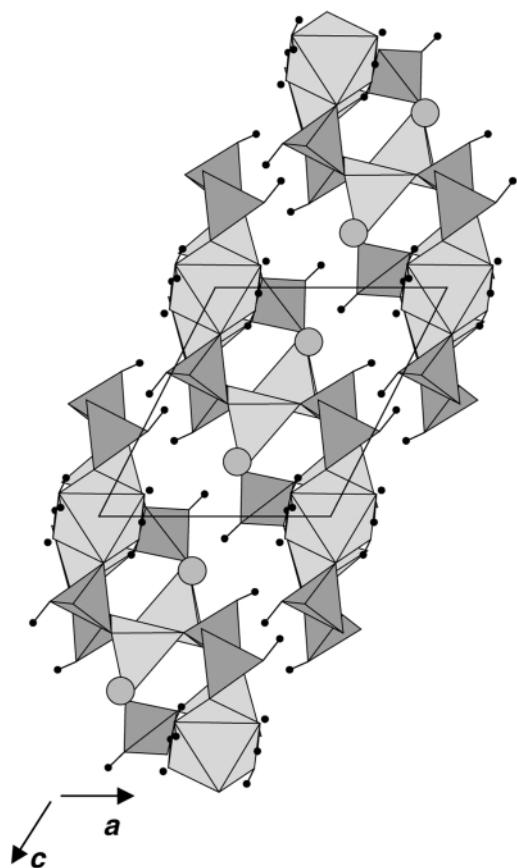


Fig. 3 The crystal structure of $\text{CsZn}_{2.5}(\text{HPO}_4)_3 \cdot 2\text{H}_2\text{O}$ is built by stacking layers, which are held together by hydrogen bonding and Cs–O bonds. Tetrahedra of PO_4 are dark, ZnO_4 and ZnO_6 are grey, hydrogen atoms are shown as small black circles, Cs atoms as larger grey circles.

Table 2 Calculated oxidation states, V_i , for cations and oxygen in the structure of $\text{CsZn}_{2.5}(\text{HPO}_4)_3 \cdot 2\text{H}_2\text{O}$, following ref. 26 and the bond lengths given in Table 1 excluding the H atoms

| | No. | V_i | CN ^a |
|-----------------|-----|-------|-----------------|
| <i>Cation</i> | | | |
| Phosphorus | 1 | 4.97 | 4 |
| | 2 | 5.10 | 4 |
| | 3 | 5.04 | 4 |
| Zinc | 1 | 2.04 | 4 |
| | 2 | 2.12 | 4 |
| | 3 | 2.05 | 6 |
| Caesium | 1 | 0.78 | 7 |
| <i>Oxygen</i> | | | |
| Framework | 2 | 2.02 | 3 |
| | 6 | 2.03 | 3 |
| | 7 | 1.99 | 3 |
| H-Bond acceptor | 11 | 1.96 | 3 |
| | 1 | 1.81 | 2 |
| | 3 | 1.72 | 2 |
| | 5 | 1.76 | 2 |
| | 8 | 1.16 | 2 |
| H-Bond donor | 9 | 1.88 | 2 |
| | 10 | 1.75 | 2 |
| | 4 | 1.20 | 1 |
| Water | 8 | 1.16 | 1 |
| | 12 | 1.17 | 1 |
| | 13 | 0.30 | 1 |
| | 14 | 0.36 | 1 |

^a CN = coordination number.

loss of crystal water as detected by TG. Another endothermic signal at 335–445 °C, $\Delta H = 39 \pm 11 \text{ kJ mol}^{-1}$ corresponds to the condensation of hydrogen phosphate and the expulsion of 1.5

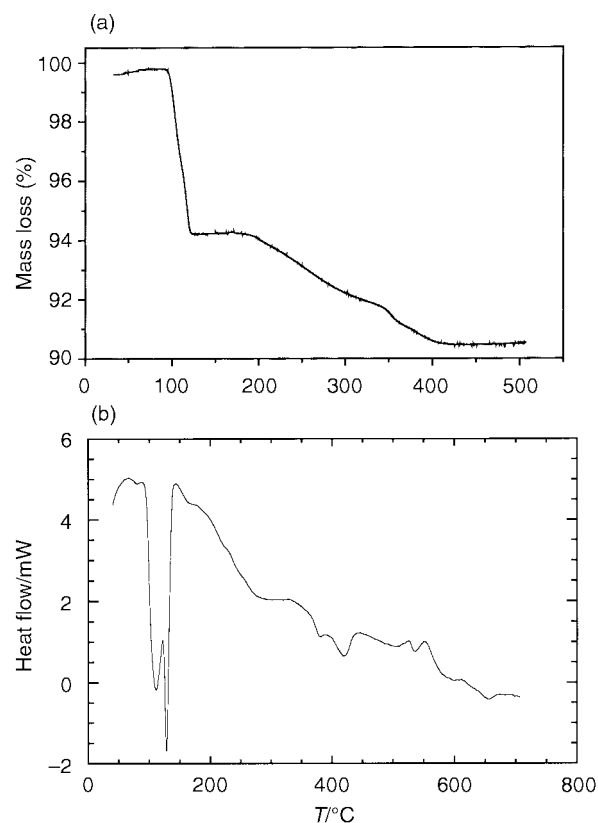


Fig. 4 Thermal investigation of $\text{CsZn}_{2.5}(\text{HPO}_4)_3 \cdot 2\text{H}_2\text{O}$: (a) the mass loss detected by thermogravimetry and (b) differential scanning calorimetry curve.

H_2O per unit of $\text{CsZn}_{2.5}(\text{HPO}_4)_3 \cdot 2\text{H}_2\text{O}$. The obtained material appears to be metastable and gives an exothermic DSC effect in the range 500–590 °C with $\Delta H = -22 \pm 6 \text{ kJ mol}^{-1}$. The thermal decomposition product has not yet been identified and might be a mixture of phases. The latter two events observed by DSC are similar to the thermal behaviour of $\text{Rb}_2\text{Zn}_2(\text{HPO}_4)_3$, but the phase transitions for $\text{CsZn}_{2.5}(\text{HPO}_4)_3 \cdot 2\text{H}_2\text{O}$ occur at higher temperature and with larger enthalpy changes.

The general tendency to form dense phases upon dry heating often limits industrial applications of open structure phosphate materials; for example catalysts often operate at temperatures higher than 300 °C.²⁷ Investigation of phases formed by dry heating of materials with open structure may lead to the discovery of new phases and knowledge which can be utilised for the design of materials with improved thermal stability.²⁸

Comparison with related materials

The system $\text{Cs}_2\text{O}-\text{ZnO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ has been explored in this work. Table 3 provides crystal data of some selected compounds related to $\text{CsZn}_{2.5}(\text{HPO}_4)_3 \cdot 2\text{H}_2\text{O}$. The three dense polymorphs of caesium zinc phosphate, CsZnPO_4 , all have the zeolite ABW structure type and the complex phase, $(\text{Cs},\text{K})_{0.33}\text{Na}_{0.18}\text{Fe}_{0.16}\text{ZnPO}_4 \cdot 1.05\text{H}_2\text{O}$, has a cancrinite type framework.^{29,30} Hydrogen phosphates often form complex crystal structures owing to hydrogen bonding, e.g. the structure of $\text{Rb}_2\text{Zn}_2(\text{HPO}_4)_3$ which is built from spiralling chains of phosphorus and zinc tetrahedra.¹² The caesium containing phases $\text{CsZn}_3(\text{HPO}_4)_2\text{PO}_4$ and $\text{CsZn}_2(\text{HPO}_4)\text{PO}_4$ have a three-dimensional framework structure and a layered structure, respectively.^{23a,31} Apparently, only three alkali metal zinc monohydrogen phosphates are known: $\text{Na}_2\text{Zn}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ (or $\text{Na}_3\text{Zn}_{1.5}(\text{HPO}_4)_3 \cdot 6\text{H}_2\text{O}$), $\text{Rb}_2\text{Zn}_2(\text{HPO}_4)_3$ and $\text{CsZn}_{2.5}(\text{HPO}_4)_3 \cdot 2\text{H}_2\text{O}$ (Table 3).^{12,32} The sodium and caesium containing phases are built from ZnO_4 and HPO_4 layers intersected by open 12- and 8-rings where the alkali ions and water molecules are placed.

Table 3 Crystal data of selected alkali metal zinc orthophosphates

| Compound | Space group | <i>a</i> /Å | <i>b</i> /Å | <i>c</i> /Å | <i>a</i> / <i>b</i> / <i>c</i> (°) | <i>V</i> /Å ³ | Ref. |
|--|-------------------------------------|-------------|-------------|-------------|------------------------------------|--------------------------|-----------|
| (Cs,K) _{0.33} Na _{0.18} Fe _{0.16} ZnPO ₄ ·1.05H ₂ O | <i>P</i> 6 ₃ | 12.49 | 12.49 | 5.00 | 90/90/120 | 676 | 30 |
| Na ₂ Zn(HPO ₄) ₂ ·4H ₂ O | <i>P</i> 2 ₁ / <i>c</i> | 8.947 | 13.254 | 10.098 | 90/116/90 | 1074.5 | 32 |
| Rb ₂ Zn ₂ (HPO ₄) ₃ | <i>P</i> 2 ₁ / <i>c</i> | 12.59 | 12.72 | 7.58 | 90/96/90 | 1207 | 12 |
| CsZn _{2.5} (HPO ₄) ₃ ·2H ₂ O | <i>P</i> 1̄ | 8.392 | 9.825 | 9.909 | 111/112/98 | 674 | This work |
| CsZn ₃ (HPO ₄) ₂ PO ₄ | <i>P</i> 1̄ | 5.16 | 8.03 | 14.80 | 96/90/108 | 581 | 23a |
| CsZn ₂ (HPO ₄) ₂ PO ₄ | <i>Abma</i> | 7.74 | 6.59 | 15.94 | 90/90/90 | 814 | 31 |
| CsZnPO ₄ | <i>P</i> 2 ₁ / <i>a</i> | 18.54 | 5.45 | 9.10 | 90/90/90 | 919 | 29 |
| CsZnPO ₄ | <i>Pn</i> 2 ₁ / <i>a</i> | 9.24 | 5.46 | 9.34 | 90/90/90 | 471 | 29 |
| CsZnPO ₄ | <i>Pnma</i> | 9.19 | 5.49 | 9.39 | 90/90/90 | 474 | 29 |

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References

- X. Bu, P. Feng and G. D. Stucky, *Science*, 1997, **278**, 2080; P. Feng, X. Bu and G. D. Stucky, *Nature (London)*, 1997, **388**, 735.
- A. Clearfield, *Chem. Mater.*, 1998, **10**, 2801; G. Alberti, M. Casciola, U. Constantino and R. Vivani, *Adv. Mater.*, 1996, **8**, 291; A. Clearfield, *Chem. Rev.*, 1988, **88**, 125; G. Alberti, U. Constantino, F. Marmottini, R. Vivani and P. Zappelli, *Microporous Mesoporous Mater.*, 1998, **21**, 297.
- Q. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schüth and G. D. Stucky, *Nature (London)*, 1994, **368**, 317.
- S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **104**, 1146; W. H. Meier and D. H. Olson, *Atlas of Zeolite Structure Types*, Butterworth-Heinemann, London, 1992.
- M. da S. Machado, D. Cardoso, J. Pérez-Pariente and E. Sastre, *Chem. Mater.*, 1999, **11**, 3238; A. Nørlund Christensen and R. G. Hazell, *Acta Chem. Scand.*, 1999, **53**, 403; see also ref. 1.
- J. M. Thomas, R. Raja, G. Sankar and R. G. Bell, *Nature (London)*, 1999, **398**, 227.
- G. Harvey and W. M. Meier, *Stud. Surf. Sci. Catal.*, 1989, **49A**, 411; T. E. Gier and G. D. Stucky, *Nature (London)*, 1991, **349**, 508; W. T. A. Harrison, T. E. Martin, T. E. Gier and G. D. Stucky, *J. Mater. Chem.*, 1992, **2**, 175.
- K. O. Kongshaug, H. Fjellvåg and K. P. Lillerud, *Chem. Mater.*, 2000, **12**, 1095; J. Escobal, J. L. Pizarro, J. L. Mesa, L. Lezama, R. Olazcuaga, M. I. Arriortua and T. Rojo, *Chem. Mater.*, 2000, **12**, 376; A. R. Cowley and A. M. Chippindale, *J. Chem. Soc., Dalton Trans.*, 1999, 2147; S. B. Harmon and S. C. Sevov, *Chem. Mater.*, 1998, **10**, 3020; A. Choudhury, S. Natarajan and C. N. R. Rao, *Chem. Mater.*, 1999, **11**, 2316; S. Ekambaram, C. Serre, G. Férey and S. C. Sevov, *Chem. Mater.*, 2000, **12**, 444; Y. Zhao, G. Zhu, X. Jiao, W. Liu and W. Pang, *J. Mater. Chem.*, 2000, **10**, 463.
- J. M. Thomas, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 913; J. Chen and J. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1994, 603.
- R. J. Francis and D. O'Hare, *J. Chem. Soc., Dalton Trans.*, 1998, 3133.
- A. Nørlund Christensen, T. R. Jensen, P. Norby and J. C. Hanson, *Chem. Mater.*, 1998, **10**, 1688; R. J. Francis, S. J. Price, S. O'Brien, A. M. Fogg, D. O'Hare, T. Loiseau and G. Férey, *Chem. Commun.*, 1997, 521.
- T. R. Jensen, R. G. Hazell, T. Vosegaard and H. J. Jakobsen, *Inorg. Chem.*, 2000, **39**, 2026.
- R. M. Barrer, *Hydrothermal Chemistry of Zeolites*, Academic Press, London 1982; see also ref. 10.
- T. R. Jensen, *J. Chem. Soc., Dalton Trans.*, 1998, 2261.
- T. R. Jensen and R. G. Hazell, *Chem. Commun.*, 1999, 371; R. H. Jones, J. Chen, G. Sankar and J. M. Thomas, *Zeolites and Related Microporous Materials: State of the Art 1994*, eds. J. Weitkamp, H. G. Karge, H. Pfeifer and W. Hölderich, *Stud. Surf. Sci. Catal.*, 1994, **84**, 2229.
- P. B. Moore and J. Shen, *Nature (London)*, 1983, **306**, 356.
- G. Y. Yang and S. C. Sevov, *J. Am. Chem. Soc.*, 1999, **121**, 8389.
- N. O. Ersson, CELLKANT, Program for unit cell refinement from powder diffraction data, Chemical Institute, Uppsala University, Uppsala, 1981.
- SMART, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1995.
- A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115.
- A. Hazell, KRYSTAL, An integrated system of crystallographic programs, Aarhus University, Denmark, 1995.
- E. Dowty, Program ATOMS version 4.0, Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA, 1997.
- (a) P. Feng, X. Bu and G. D. Stucky, *Acta Crystallogr., Sect. C*, 1997, **53**, 1170; (b) J. A. McGinney, *Inorg. Chem.*, 1974, **13**, 1057.
- S. Oliver, A. Kuperman, A. Lough and G. A. Ozin, *Chem. Mater.*, 1996, **8**, 2391.
- J. V. Smith, *Chem. Rev.*, 1988, **88**, 149.
- I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B*, 1985, **41**, 244.
- P. B. Venuto, *Microporous Mater.*, 1994, **2**, 297.
- J. Gopalakrishnan, *Chem. Mater.*, 1995, **7**, 1265.
- D. Blum, A. Durif and M. T. Averbuch-Pouchot, *Ferroelectrics*, 1986, **69**, 283.
- O. V. Yakubovich, O. V. Karimova and O. K. Mel'nikov, *Crystallogr. Rep. (Engl. Transl.)*, 1994, **39**, 564.
- T. M. Nenoff, W. T. A. Harrison, T. E. Gier, J. C. Calabrese and G. D. Stucky, *J. Solid State Chem.*, 1993, **107**, 285.
- W. T. A. Harrison, T. M. Nenoff, T. E. Gier and G. D. Stucky, *J. Solid State Chem.*, 1994, **113**, 168.