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New layered caesium zinc hydrogen phosphate, $CsZn_{2.5}(HPO_4)_3$·$2H_2O$; synthesis, crystal structure and thermal transformation

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The synthesis, crystal structure and thermal transformation of a new caesium zinc hydrogen phosphate hydrate, $CsZn_{2.5}(HPO_4)_3$·$2H_2O$, 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 $CsZn_{2.5}(HPO_4)_3$·$2H_2O$ 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, $[C_nH_{2n+1}NMe_3Br]$·$ZnHPO_4$ 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.* $Al^{3+} \longrightarrow Zn^{2+} + M^+$ 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, M_2O·P_2O_5·amine·H_2O.[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 adsorbtion.[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.* $Rb_2Zn_2(HPO_4)_3$ crystallised after 4.5 months at 52 °C.[12] Successive phase transformations can be observed upon prolonged thermal treatment where the phases formed have higher thermodynamic stability,[13] *e.g.* β-$LiZnPO_4$·H_2O, prepared by solution mediated conversion of α-$LiZnPO_4$·H_2O, a phase with 2.5% lower density.[14] We have also discovered a templated zinc phosphate, $LiZn(HPO_4)(PO_4)$·$NH_3CH_2CH_2NH_3$·H_2O, which crystallised after *ca.* 3 months at room temperature by solvothermal conversion of a microporous material, $Zn_2(PO_4)_2$·$NH_3CH_2CH_2NH_3$, 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, $CsZn_{2.5}(HPO_4)_3$·$2H_2O$.

Experimental

Hydrothermal synthesis

The system, Cs_2O–ZnO–P_2O_5–H_2O, 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 $Zn(MeCO_2)_2$·$2H_2O$ (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,

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>99%), 50% CsOH (Aldrich, 99%), 85% H_3PO_4 (Fluka, extra pure, >98%), $Zn(MeCO_2)_2 \cdot 2H_2O$ (Fluka, *purum* p.a. >99.0%) and $MeCO_2H$ (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-Kα_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 $CsZn_{2.5}(HPO_4)_3 \cdot 2H_2O$ ($0.10 \times 0.10 \times 0.03$ mm) was used for the data collection performed on a Siemens SMART diffractometer equipped with a CCD detector and graphite monochromated Mo-Kα 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. $CsZn_{2.5}(HPO_4)_3 \cdot 2H_2O$, $M = 620.34$, triclinic, space group $P\bar{1}$ (no. 2) $a = 8.3918(6)$, $b = 9.8254(8)$, $c = 9.9090(7)$ Å, $\alpha = 111.172(1)$, $\beta = 111.751(1)$, $\gamma = 97.560(1)°$, $U = 673.59$ Å^3, $T = 120$ K, $Z = 2$, μ(Mo-Kα) = 7.52 mm^{-1}, 17148 reflections measured, 2340 unique reflections ($R_{int} = 0.021$) 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 Al_2O_3 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, Al_2O_3. 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 $CsZn_3(HPO_4)_2PO_4$ (*ca.* 95%) and polyhedra of an orthorhombic caesium zinc chloride, Cs_2ZnCl_4, where obtained from portion A (heated to 150 °C for 5 days).[23] A small amount of thin needle shaped crystals of $CsZn_3(HPO_4)_2PO_4$ along with semi-amorphous material were recovered from portion B (52 °C, 6 months).[23a]

Crystallisation of the new layered caesium zinc hydrogenphosphate, $CsZn_{2.5}(HPO_4)_3 \cdot 2H_2O$ discovered in this work was noticed after 2 months at room temperature (portion C) [triclinic, $a = 8.388(1)$, $b = 9.830(2)$, $c = 9.907(1)$ Å, $\alpha = 111.21(1)$, $\beta = 111.70(1)$ and $\gamma = 97.56(1)°$, $U = 673.5(2)$ Å^3, 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 $CsZn_{2.5}(HPO_4)_3 \cdot 2H_2O$ formed after a nucleation period of two months. The phase stability field of $CsZn_{2.5}(HPO_4)_3 \cdot 2H_2O$ 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 $CsZn_{2.5}(HPO_4)_3 \cdot 2H_2O$

The crystal structure of $CsZn_{2.5}(HPO_4)_3 \cdot 2H_2O$ is built from regular tetrahedra of PO_4 and ZnO_4 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 $Zn(1,2)O_4$ and $P(1,3)O_4$ 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 $P(2)O_4$ tetrahedra to form a layer illustrated in Fig. 1 as a *b*,*c* projection of the crystal structure of $CsZn_{2.5}(HPO_4)_3 \cdot 2H_2O$. 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 $CsZn_{2.5}(HPO_4)_3 \cdot 2H_2O$ 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 $CsZn_{2.5}(HPO_4)_3 \cdot 2H_2O$

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)			O6–Cs–O11	58.0(1)
Zn3–O14	2.202(4)	O13–Zn3–O14	90.5(2)	O4–H4	0.64(8)	O6–Cs–O12	89.7(1)
Mean	2.113			O8–H8	0.99(7)	O6–Cs–O8	164.8(1)
				O12–H12	1.11(8)	O7–Cs–O14	132.1(1)
P1–O2	1.516(4)	O1–P1–O2	113.4(2)	O13–H13*a*	0.87(6)	O7–Cs–O11	69.5(1)
P1–O1	1.528(4)	O2–P1–O3	110.5(2)	O13–H13*b*	1.17(12)	O7–Cs–O12	84.2(1)
P1–O3	1.540(4)	O2–P1–O4	104.2(2)	O14–H14*a*	0.99(10)	O7–Cs–O8	70.4(1)
P1–O4	1.563(5)	O1–P1–O3	109.2(2)	O14–H14*b*	0.79(9)	O8–Cs–O11	128.97(9)
Mean	1.537	O1–P1–O4	110.4(2)				
		O3–P1–O4	108.9(2)	H8–O5	1.58(7)	O8–Cs–O12	103.6(1)
				H12–O10	1.60(8)	O8–Cs–O12	103.6(1)
P2–O6	1.479(4)	O5–P2–O6	112.0(2)	H14*a*–O8	1.80(10)	O8–Cs–O14	140.7(1)
P2–O5	1.535(4)	O6–P2–O7	113.8(2)	H13*b*–O1	1.91(12)	O11–Cs–O12	42.34(9)
P2–O7	1.517(4)	O6–P2–O8	106.5(2)	H13*a*–O9	1.97(7)	O11–Cs–O14	62.8(1)
P2–O8	1.585(4)	O5–P2–O7	107.6(2)	H4–O3	2.06(8)	O12–Cs–O14	57.6(1)
Mean	1.529	O5–P2–O8	107.1(2)				
		O7–P2–O8	109.5(2)				

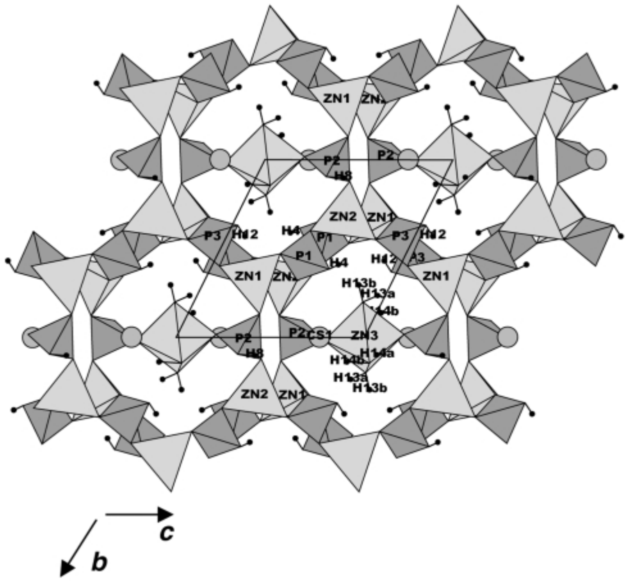

Fig. 1 The crystal structure of $CsZn_{2.5}(HPO_4)_3 \cdot 2H_2O$ shown as a *b*,*c*-projection; 4-ring chains of alternating $Zn(1,2)O_4$ and $P(1,3)O_4$ tetrahedra propagating in the *c* direction are connected by $P(2)O_4$. The Zn(3) octahedra are placed across pseudo 12-ring openings and coordinate to water oxygens. 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.

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 $CsZn_{2.5}(HPO_4)_3 \cdot 2H_2O$ 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 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 H_2O per unit of $CsZn_{2.5}(HPO_4)_3 \cdot 2H_2O$ (theoretical mass loss 4.4%).

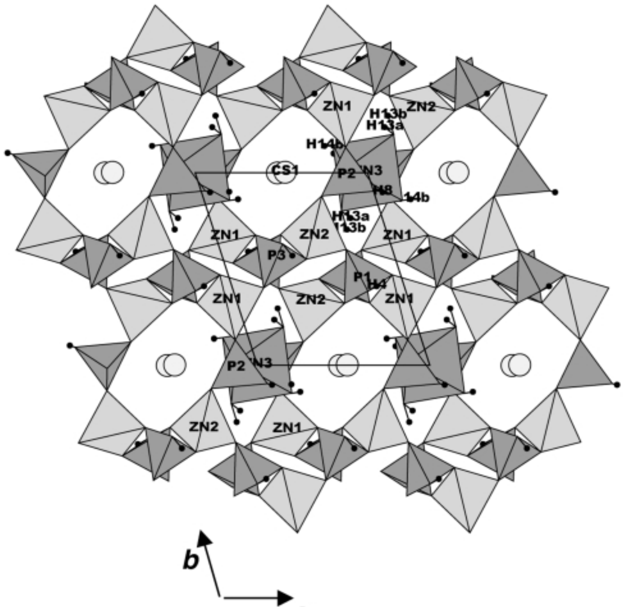

Fig. 2 An *a*,*b*-projection of the crystal structure of $CsZn_{2.5}(HPO_4)_3 \cdot 2H_2O$ reveal 8-ring openings with caesium placed above and below. Tetrahedra of PO_4 are dark, ZnO_4 and ZnO_6 are grey, hydrogen atoms are shown as small black circles, Cs atoms as larger grey circles.

Differential scanning calorimetry of $CsZn_{2.5}(HPO_4)_3 \cdot 2H_2O$ 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

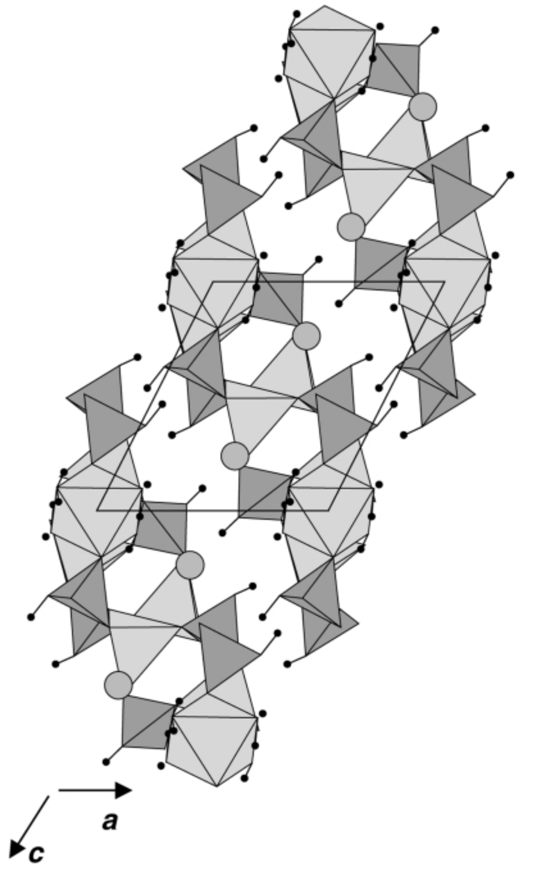

Fig. 3 The crystal structure of $CsZn_{2.5}(HPO_4)_3{\cdot}2H_2O$ is built by stacking layers, which are held together by hydrogen bonding and Cs–O bonds. Tetrahedra of PO_4 are dark, ZnO_4 and ZnO_6 are grey, hydrogen atoms are shown as small black circles, Cs atoms as larger grey circles.

Table 2 Calculated oxidation states, V_i, for cations and oxygen in the structure of $CsZn_{2.5}(HPO_4)_3{\cdot}2H_2O$, following ref. 26 and the bond lengths given in Table 1 excluding the H atoms

	No.	V_i	CN[a]
Cation			
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
Oxygen			
Framework	2	2.02	3
	6	2.03	3
	7	1.99	3
	11	1.96	3
H-Bond acceptor	1	1.81	2
	3	1.72	2
	5	1.76	2
	8	1.16	2
	9	1.88	2
	10	1.75	2
H-Bond donor	4	1.20	1
	8	1.16	1
	12	1.17	1
Water	13	0.30	1
	14	0.36	1

[a] CN = coordination number.

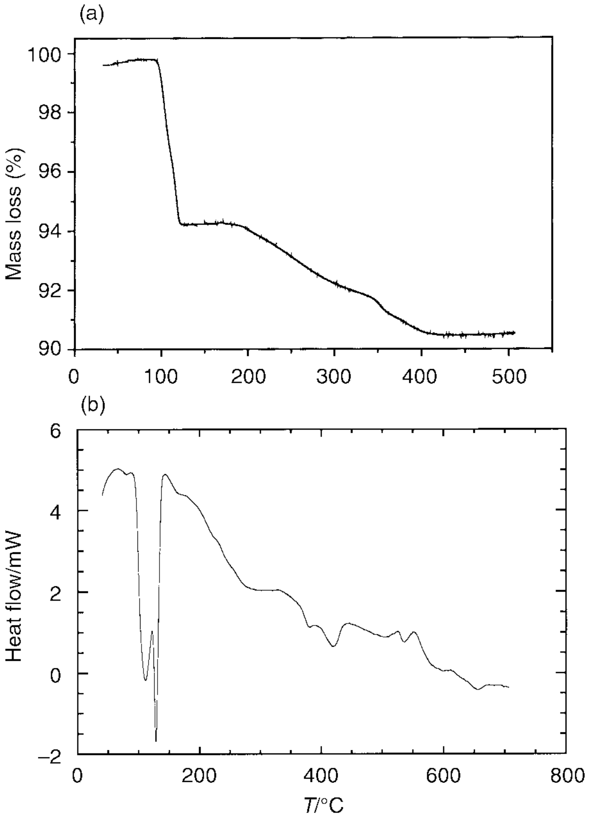

Fig. 4 Thermal investigation of $CsZn_{2.5}(HPO_4)_3{\cdot}2H_2O$: (*a*) the mass loss detected by thermogravimetry and (*b*) differential scanning calorimetry curve.

loss of crystal water as detected by TG. Another endothermic signal at 335–445 °C, $\Delta H = 39 \pm 11$ kJ mol^{-1} corresponds to the condensation of hydrogen phosphate and the expulsion of 1.5 H_2O per unit of $CsZn_{2.5}(HPO_4)_3{\cdot}2H_2O$. The obtained material appears to be metastable and gives an exothermic DSC effect in the range 500–590 °C with $\Delta H = -22 \pm 6$ 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 $Rb_2Zn_2(HPO_4)_3$, but the phase transitions for $CsZn_{2.5}(HPO_4)_3{\cdot}2H_2O$ 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 Cs_2O–ZnO–P_2O_5–H_2O has been explored in this work. Table 3 provides crystal data of some selected compounds related to $CsZn_{2.5}(HPO_4)_3{\cdot}2H_2O$. The three dense polymorphs of caesium zinc phosphate, $CsZnPO_4$, all have the zeolite ABW structure type and the complex phase, $(Cs,K)_{0.33}Na_{0.18}Fe_{0.16}ZnPO_4{\cdot}1.05H_2O$, has a cancrinite type framework.[29,30] Hydrogen phosphates often form complex crystal structures owing to hydrogen bonding, *e.g.* the structure of $Rb_2Zn_2(HPO_4)_3$ which is built from spiralling chains of phosphorus and zinc tetrahedra.[12] The ceasium containing phases $CsZn_3(HPO_4)_2PO_4$ and $CsZn_2(HPO_4)PO_4$ have a three-dimensional framework structure and a layered structure, respectively.[23a,31] Apparently, only three alkali metal zinc monohydrogen phosphates are known: $Na_2Zn(HPO_4)_2{\cdot}4H_2O$ (or $Na_3Zn_{1.5}(HPO_4)_3{\cdot}6H_2O$), $Rb_2Zn_2(HPO_4)_3$ and $CsZn_{2.5}(HPO_4)_3{\cdot}2H_2O$ (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	a/Å	b/Å	c/Å	$\alpha/\beta/\gamma$(°)	V/Å^3	Ref.
$(Cs,K)_{0.33}Na_{0.18}Fe_{0.16}ZnPO_4\cdot1.05H_2O$	$P6_3$	12.49	12.49	5.00	90/90/120	676	30
$Na_2Zn(HPO_4)_2\cdot4H_2O$	$P2_1/c$	8.947	13.254	10.098	90/116/90	1074.5	32
$Rb_2Zn_2(HPO_4)_3$	$P2_1/c$	12.59	12.72	7.58	90/96/90	1207	12
$CsZn_{2.5}(HPO_4)_3\cdot2H_2O$	$P\bar{1}$	8.392	9.825	9.909	111/112/98	674	This work
$CsZn_3(HPO_4)_2PO_4$	$P\bar{1}$	5.16	8.03	14.80	96/90/108	581	23*a*
$CsZn_2(HPO_4)PO_4$	*Abma*	7.74	6.59	15.94	90/90/90	814	31
$CsZnPO_4$	$P2_1/a$	18.54	5.45	9.10	90/90/90	919	29
$CsZnPO_4$	$Pn2_1a$	9.24	5.46	9.34	90/90/90	471	29
$CsZnPO_4$	*Pnma*	9.19	5.49	9.39	90/90/90	474	29

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References

1 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.

2 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.

3 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.

4 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.

5 M. da S. Machado, D. Cardoso, J. Pèrez-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.

6 J. M. Thomas, R. Raja, G. Sankar and R. G. Bell, *Nature* (*London*), 1999, **398**, 227.

7 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.

8 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.

9 J. M. Thomas, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 913; J. Chen and J. M. Thomas, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 603.

10 R. J. Francis and D. O'Hare, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 3133.

11 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.

12 T. R. Jensen, R. G. Hazell, T. Vosegaard and H. J. Jakobsen, *Inorg. Chem.*, 2000, **39**, 2026.

13 R. M. Barrer, *Hydrothermal Chemistry of Zeolites*, Academic Press, London 1982; see also ref. 10.

14 T. R. Jensen, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 2261.

15 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.

16 P. B. Moore and J. Shen, *Nature* (*London*), 1983, **306**, 356.

17 G. Y. Yang and S. C. Sevov, *J. Am. Chem. Soc.*, 1999, **121**, 8389.

18 N. O. Ersson, CELLKANT, Program for unit cell refinement from powder diffraction data, Chemical Institute, Uppsala University, Uppsala, 1981.

19 SMART, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1995.

20 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.

21 A. Hazell, KRYSTAL, An integrated system of crystallographic programs, Aarhus University, Denmark, 1995.

22 E. Dowty, Program ATOMS version 4.0, Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA, 1997.

23 (*a*) P. Feng, X. Bu and G. D. Stucky, *Acta Crystallogr.*, *Sect. C*, 1997, **53**, 1170; (*b*) J. A. McGinnety, *Inorg. Chem.*, 1974, **13**, 1057.

24 S. Oliver, A. Kuperman, A. Lough and G. A. Ozin, *Chem. Mater.*, 1996, **8**, 2391.

25 J. V. Smith, *Chem. Rev.*, 1988, **88**, 149.

26 I. D. Brown and D. Altermatt, *Acta Crystallogr.*, *Sect. B*, 1985, **41**, 244.

27 P. B. Venuto, *Microporous Mater.*, 1994, **2**, 297.

28 J. Gopalakrishnan, *Chem. Mater.*, 1995, **7**, 1265.

29 D. Blum, A. Durif and M. T. Averbuch-Pouchot, *Ferroelectrics*, 1986, **69**, 283.

30 O. V. Yakubovich, O. V. Karimova and O. K. Mel'nikov, *Crystallogr. Rep.*(*Engl. Transl.*), 1994, **39**, 564.

31 T. M. Nenoff, W. T. A. Harrison, T. E. Gier, J. C. Calabrese and G. D. Stucky, *J. Solid State Chem.*, 1993, **107**, 285.

32 W. T. A. Harrison, T. M. Nenoff, T. E. Gier and G. D. Stucky, *J. Solid State Chem.*, 1994, **113**, 168.