

A new polymorph of $\text{LiZnPO}_4 \cdot \text{H}_2\text{O}$; synthesis, crystal structure and thermal transformation †

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A new polymorph of lithium zinc phosphate hydrate, $\beta\text{-LiZnPO}_4 \cdot \text{H}_2\text{O}$, has been obtained by hydrothermal synthesis, and its crystal structure and thermal transformation investigated. The crystal structure can be viewed as a framework structure built from PO_4 and ZnO_4 tetrahedra with LiO_4 tetrahedra and water molecules placed in eight-ring channels; $\beta\text{-LiZnPO}_4 \cdot \text{H}_2\text{O}$ is apparently the only member of the zeolite ABW group of materials crystallising in space group $P2_1ab$. It has a doubled b axis compared to a known phase of $\text{LiZnPO}_4 \cdot \text{H}_2\text{O}$. The ^{31}P MAS NMR spectrum showed two signals; δ 6.94(2) and 7.88(2). The known phase of $\text{LiZnPO}_4 \cdot \text{H}_2\text{O}$ transforms into $\beta\text{-LiZnPO}_4 \cdot \text{H}_2\text{O}$ after treatment in 0.9 M LiNO_3 (aq) at 80 °C and 10 kbar for 20 h. A mechanism for the pressure-induced displacive phase transition is proposed. Dry or hydrothermal heating of $\beta\text{-LiZnPO}_4 \cdot \text{H}_2\text{O}$ at >100 °C gave $\delta_1\text{-LiZnPO}_4$. The enthalpy change for the dehydration with a maximum at 219(2) °C was determined to be $\Delta H = 43(6)$ kJ mol $^{-1}$, using differential scanning calorimetry.

Microporous materials have found extensive industrial use over the last decades, e.g. as gas absorbers, ion exchangers, catalysts and many other applications.¹ Such materials with new framework structures and compositions are of great importance as their function is often correlated with the internal shape and size of cages and channels and the position of metal ions in the material. Among new materials a large number of phosphates and some arsenates have been characterised during the last decade.²

The chemistry of zinc orthophosphates shows a large variety of phases mainly due to the co-ordination flexibility of the zinc ions and their ability to form Zn–O–Zn linkages.³ An increasing number of orthophosphates are found in the system, ZnO–P $_2$ O $_5$ -cation, prepared by hydrothermal synthesis from aqueous or non-aqueous solutions using alkali-metal ions and/or organic amine ions as templates. There are several members of this group which are structural analogues to aluminosilicates, e.g. sodalite, zeolite-X and ABW,⁴ but also compounds with novel crystal structures with no naturally occurring mineral counterpart, e.g. $\text{Zn}_2(\text{HPO}_4)_3 \cdot \text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3$.⁵ A member of this family, $\text{Zn}(\text{H}_2\text{PO}_4)(\text{HPO}_4) \cdot (\text{CH}_3)_4\text{N}$, possesses very low framework density, 10.1 tetrahedral framework atoms (T) per 1000 Å 3 .⁶ In general microporous materials are metastable as they transform to more dense phases upon heating either dry or hydrothermal. Careful adjustment of synthesis conditions is crucial for preparation of new materials, e.g. stabilisation and isolation of intermediate phases in the synthesis of more dense phases.

Hydrothermal preparation techniques have revealed the existence of several new lithium zinc phosphates and the crystallisation fields of the compounds are under further investigation.⁷ A polymorph of LiZnPO_4 having a phenacite type structure (denoted $\varepsilon\text{-LiZnPO}_4$ in this work for distinction from the other polymorphs),⁸ a cristobalite related phase, $\delta_1\text{-LiZnPO}_4$,⁹ and a polymorph (denoted $\alpha'\text{-LiZnPO}_4$)⁷ with a more complex crystal structure can all be prepared by hydrothermal methods. The compound $\alpha'\text{-LiZnPO}_4$ is possibly structurally related to $\alpha\text{-LiZnPO}_4$,⁷ which is the stable phase under ambient conditions prepared by solid state reaction. A common feature of the lithium zinc phosphates, α -, ε - and $\delta_1\text{-LiZnPO}_4$ (and possibly also $\alpha'\text{-LiZnPO}_4$), are three-dimensional framework structures built from LiO_4 , ZnO_4 and PO_4 tetrahedra forming

six-ring channels.^{7–10} The system $\text{Li}_3\text{PO}_4\text{-Zn}_3(\text{PO}_4)_2$ was studied by means of solid state reactions and thermal analysis. The equilibrium phase diagram shows the existence of four lithium zinc phosphates with the compositions $\text{Li}_4\text{Zn}(\text{PO}_4)_2$, $\text{Li}_9\text{Zn}_6(\text{PO}_4)_7$, LiZnPO_4 and ' $\text{LiZn}_9(\text{PO}_4)_7$ ', and each of them may exist in one, two or three modifications. The phase diagram reveals that $\alpha\text{-LiZnPO}_4$ transforms to $\beta\text{-LiZnPO}_4$ at 737 °C, $\gamma\text{-LiZnPO}_4$ at 1006 °C and melts at 1172 °C.¹¹ It is not possible to quench β - or $\gamma\text{-LiZnPO}_4$ to ambient conditions as the phase transitions are reversible and the only available structural data is a powder pattern of $\beta\text{-LiZnPO}_4$.^{9b} A polymorph of $\text{Li}_4\text{-Zn}(\text{PO}_4)_2$ and the mentioned phases of LiZnPO_4 seem to be the only compositions from the phase diagram that can be prepared by means of hydrothermal synthesis.¹²

A water-containing lithium zinc phosphate, $\text{LiZnPO}_4 \cdot \text{H}_2\text{O}$, was described having a zeolite type ABW structure, i.e. isomorphous with zeolite Li-A(BW), $\text{LiAlSiO}_4 \cdot \text{H}_2\text{O}$.^{9a} An accurate structure analysis of $\text{LiAlSiO}_4 \cdot \text{H}_2\text{O}$ was performed by combining single crystal and powder diffraction data, using X-rays and neutron radiation, respectively.¹³ The structure can be viewed as a framework built from AlO_4 and SiO_4 tetrahedra giving four- and eight-ring channels in the crystallographic c direction and six-ring channels in a perpendicular direction. The lithium ions are co-ordinated to three framework oxygen atoms and one water oxygen atom.¹³

The polymorph of $\text{LiZnPO}_4 \cdot \text{H}_2\text{O}$ ^{9a} found to be isomorphous with zeolite ABW is denoted $\alpha\text{-LiZnPO}_4 \cdot \text{H}_2\text{O}$ in the following. The polymorph of $\text{LiZnPO}_4 \cdot \text{H}_2\text{O}$ discovered in this study has similar unit cell parameters to those of $\alpha\text{-LiZnPO}_4 \cdot \text{H}_2\text{O}$, but the b axis is doubled, therefore, denoted $\beta\text{-LiZnPO}_4 \cdot \text{H}_2\text{O}$. The synthesis, crystal structure and thermal properties of $\beta\text{-LiZnPO}_4 \cdot \text{H}_2\text{O}$ are now reported.

Experimental

Hydrothermal synthesis

In a search for new materials the system $\text{Li}_2\text{O-ZnO-P}_2\text{O}_5$ -template was investigated by hydrothermal synthesis in aqueous and non-aqueous solutions using organic amine ions as templates. A synthesis was performed by dissolving $\text{LiOH} \cdot \text{H}_2\text{O}$ (3.677 g), LiCl (3.709 g) and $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ (18.971 g) in water (100 cm 3). Phosphoric acid, 85% H_3PO_4 (10.0 cm 3), and then ethyldiisopropylamine (30.0 cm 3) was slowly added with stirring giving a molar ratio of the reactants $\text{Li:Zn:PO}_4\text{:NETPr}_2\text{:water}$ of 1.2:0.6:1:1.2:~41, $[\text{PO}_4] \approx 0.9$ M, pH 4.55

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† Non-SI unit employed: bar = 101 325 Pa.

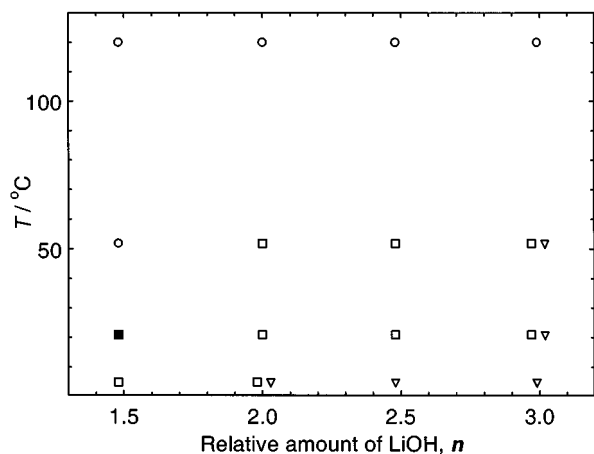


Fig. 1 The crystallisation fields of lithium zinc orthophosphates formed in the system $\text{LiOH-Zn}(\text{CH}_3\text{CO}_2)_2\text{-H}_3\text{PO}_4\text{-water}$, at varying amounts of LiOH , n , and temperature. In one case a phase-pure sample of $\beta\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$ (■) was obtained. Open symbols indicate impurities of $\beta\text{-Li}_3\text{PO}_4$, and $\alpha\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$ is shown as triangles, $\beta\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$ as squares and $\alpha'\text{-LiZnPO}_4$ as circles

(measured 1 h after mixing). After stirring the gel for 1 h, powder diffraction showed the presence of $\alpha\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$ of poor crystallinity along with a trace of an unidentified phase. A portion of the gel, *ca.* 5 cm^3 , was left to stand for 3 months at room temperature, *ca.* $21\text{ }^\circ\text{C}$, before crystallisation was noticed and after 6 months the crystallisation was complete and the material (Sample I) was recovered by filtration and washed with deionised water. Another portion of the gel was heated at $55\text{ }^\circ\text{C}$ for 3 months giving $\alpha\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$ as product. The rest of the gel was heated to $200\text{ }^\circ\text{C}$ for 68 h in a Teflon-lined steel autoclave giving $\delta_1\text{-LiZnPO}_4$ as product.

In order to investigate the crystallisation fields of lithium zinc phosphates formed in the system $\text{LiOH-Zn}(\text{CH}_3\text{CO}_2)_2\text{-H}_3\text{PO}_4\text{-water}$, a number of syntheses were performed varying the amount of LiOH and the temperature. The LiOH and $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ were dissolved in water and H_3PO_4 was slowly added with stirring forming a white gel. The relative amount of lithium is given as a variable n , relative to the amount of phosphoric acid: $n = n(\text{Li})/n(\text{PO}_4)$. The molar composition of the synthesis mixtures, $\text{Li}:\text{Zn}:\text{PO}_4:\text{H}_2\text{O}$, was $n:0.52:1:\approx 20$, where $n = 1.49, 2.00, 2.48$ or 2.99 , $[\text{PO}_4] \approx 1.8\text{ M}$, $4.0 < \text{pH} < 7.2$, thermal treatment at $5, 21$ or $52\text{ }^\circ\text{C}$ for 28 d and at $120\text{ }^\circ\text{C}$ for 6 d. The phase identification was performed by combining information from ^{31}P MAS NMR and powder diffraction and the products are displayed in Fig. 1. In one case a phase-pure sample of $\beta\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$ was obtained (filled square) and the other samples contained impurities of $\beta\text{-Li}_3\text{PO}_4$ (open symbols). At high temperatures, *e.g.* $120\text{ }^\circ\text{C}$, $\alpha'\text{-LiZnPO}_4$ (circles) formed and at low temperatures $\alpha\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$ (triangles) was found as product. Optimisation of the conditions for the hydrothermal synthesis revealed that templates were in fact not essential for the preparation of $\beta\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$. Several syntheses in the system $\text{LiOH-LiCl-Zn}(\text{CH}_3\text{CO}_2)_2\text{-H}_3\text{PO}_4\text{-(CH}_2\text{OH)}_2$ were performed in a similar way substituting the solvent water with ethylene glycol but gave only semiamorphous material with traces of $\alpha'\text{-LiZnPO}_4$ and $\beta\text{-Li}_3\text{PO}_4$ as products.

A Teflon container holding a suspension of $\alpha\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$ (0.381 g) in 0.9 M LiNO_3 (aq) (10 cm^3) and H_3PO_4 (0.1 cm^3) were heated in a PSIKA 20 kbar reactor at $80\text{ }^\circ\text{C}$ and 10 kbar for 20 h, using oil as supporting fluid. The composition of the suspension was $\text{Li}:\text{Zn}:\text{PO}_4:\text{water} = 2.6:0.58:1:\approx 142$. The product was washed with ethanol (99.9%) and identified as $\beta\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$ using powder diffraction.

A Radiometer glass electrode combined with a calomel reference electrode (GK2401C) was used for pH measurements. The syntheses were performed using the following commercial chemicals: $\text{LiOH}\cdot\text{H}_2\text{O}$ (Fluka, puriss p.a., >99%), LiNO_3

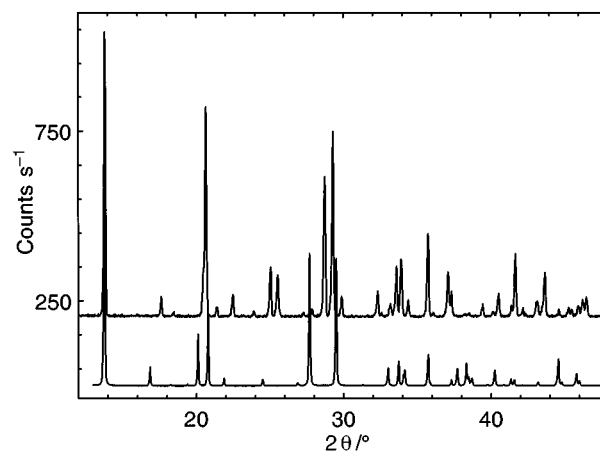


Fig. 2 Powder X-ray diffraction patterns of $\alpha\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$ (bottom) and $\beta\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$

(Merck, >98%), LiCl (Merck, pro analysi, >99%), H_3PO_4 (85%, Fluka, extra pure), $\text{Zn}(\text{CH}_3\text{CO}_2)_2\cdot 2\text{H}_2\text{O}$ (Fluka, purum p.a. >99.0%), ethyldiisopropylamine (Aldrich, >99%) and ethylene glycol (Fluka, puriss p.a., >99.5%).

Powder diffraction

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 ($\text{Cu-K}\alpha_1$ radiation, $\lambda = 1.540\ 598\ \text{\AA}$). The data were collected from 5 and up to 90° in 2θ with a step length of 0.02° and counting time of 2–15 s per step. The observed powder pattern of $\beta\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$ was distinctly different from that of the known zeolite type ABW polymorph, $\alpha\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$, as shown in Fig. 2. The trial and error indexing program TREOR¹⁴ revealed an orthorhombic unit cell of $\beta\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$ similar to the unit cell of $\alpha\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$ with a doubled b axis. The program CELLKANT¹⁵ was used to refine the unit cell parameters from the observed d spacings. The indexed powder pattern of $\beta\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$ (39 reflections, $I/I_0 > 2\%$) is given in Table 1 using the refined unit cell dimensions of $\beta\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$, $a = 10.030(1)$, $b = 16.553(2)$ and $c = 5.0120(5)\ \text{\AA}$, unit cell volume = $832.1(2)\ \text{\AA}^3$.

Single crystal diffraction

A clear, colourless octahedron of $\beta\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$ was selected from sample I. The data collection was performed on a Siemens SMART diffractometer equipped with a CCD detector and graphite monochromatised $\text{Mo-K}\alpha$ radiation, $\lambda = 0.710\ 73\ \text{\AA}$. Approximately one hemisphere of data was collected in frames covering 0.3° in ω in three sets at different ϕ angles using a detector to crystal distance of 40.0 mm . Data were corrected for Lorentz-polarisation effects and for absorption using Gaussian integration [transmission (maximum/minimum) $0.6383/0.3748$] giving 1359 unique reflections.

A structural model was found using direct methods in space group $P2_1ab$, no. 29. This setting was chosen to resemble the unit cell of $\alpha\text{-LiZnPO}_4\cdot\text{H}_2\text{O}$ refined in space group $Pna2_1$, no. 33.^{9a} Programs from the Siemens SHELXTLTM software package were used for structure solution and refinement.¹⁶ After anisotropic refinement it was possible to locate the positions of the four hydrogen atoms in the Fourier-difference maps. The H atom positions and thermal parameters were not refined; all other atoms were refined with anisotropic thermal parameters. Scattering factors of neutral atoms were applied throughout. The refinement converged at $R = 0.0290$ and $R' = 0.0717$, with 146 parameters refined using full-matrix least squares based on all F^2 . Atomic coordinates are shown in Table 2. Drawings of the crystal structure were prepared using the program ATOMS.¹⁷

Table 1 Indexed powder pattern of β -LiZnPO₄·H₂O

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{calc} /Å	<i>d</i> _{obs} /Å	(<i>I</i> / <i>I</i>) _{calc}	(<i>I</i> / <i>I</i>) _{obs}
1	2	0	6.3838	6.3834	100	100
2	0	0	5.0152	5.0173	4	7
1	1	1	4.3275	4.3299	12	7
0	2	1	4.2872	4.2842	79	74
0	4	0	4.1382	4.1438	3	4
1	2	1	3.9422	3.9433	6	6
2	0	1	3.5452	3.5451	22	18
1	3	1	3.4796	3.4827	16	15
2	4	0	3.1919	3.1938	2	3
3	2	0	3.1001	3.1009	58	49
1	4	1	3.0409	3.0426	69	65
2	3	1	2.9826	2.9826	8	7
0	5	1	2.7623	2.7644	9	9
2	4	1	2.6923	2.6918	5	4
1	5	1	2.6632	2.6629	16	18
3	2	1	2.6365	2.6352	24	21
3	4	0	2.6007	2.6012	7	6
0	0	2	2.5060	2.5074	32	30
2	5	1	2.4196	2.4194	16	16
1	1	2	2.4055	2.4052	8	7
0	3	2	2.2817	2.2818	5	4
2	1	2	2.2214	2.2229	8	9
2	2	2	2.1645	2.1649	22	22
0	7	1	2.1386	2.1384	2	3
1	7	1	2.0916	2.0916	8	6
0	8	0	2.0691	2.0688	14	15
4	4	1	1.9717	1.9712	3	4
3	6	1	1.9587	1.9593	5	6
3	2	2	1.9489	1.9498	6	7
4	6	0	1.8562	1.8562	7	8
2	8	1	1.7870	1.7869	6	5
4	6	1	1.7402	1.7399	8	8
4	3	2	1.6876	1.6880	5	5
5	6	0	1.6225	1.6224	7	7
0	8	2	1.5955	1.5957	6	7
6	0	1	1.5858	1.5856	9	7
1	3	3	1.5790	1.5784	5	8
2	10	0	1.5719	1.5720	13	11
4	5	2	1.5627	1.5627	5	5

Crystal data. LiO₄PZn·H₂O, *M* = 185.30, orthorhombic, space group *P*2₁*ab* (no. 29), *a* = 10.0224(9), *b* = 16.5596(15), *c* = 5.0126(5) Å, *U* = 831.93(13) Å³, *D*_c = 2.959, *D*_m = 3.01 g cm⁻³ (measured using a pycnometer and water), *T* = 293 K, *Z* = 8, μ(Mo-Kα) = 6.189 mm⁻¹, 3348 reflections measured, 1359 unique (*R*_{int} = 0.0362).

CCDC reference number 186/1004.

See <http://www.rsc.org/suppdata/dt/1998/2261/> for crystallographic files in .cif format.

Spectroscopic investigation

Magic angle spinning ³¹P NMR spectra were recorded on a Varian UNITY-500 spectrometer [11.7 T, ν(³¹P) = 202.332 MHz], using a Jakobsen MAS probe.¹⁸ The samples were placed in a cylindrical rotor (Si₃N₄, 5 mm outside diameter, volume 220 μl). The free induction decays were recorded with a spinning speed of 5.5 kHz and the resulting spectra had a digital resolution of 2.5 Hz. An aqueous solution of H₃PO₄ (85%, Fluka, extra pure) was used as external standard. Infrared spectra were measured on a Perkin-Elmer 1720 Fourier-transform spectrometer using pellets of KBr containing 1% of the compound. The spectral resolution was 4 cm⁻¹.

Thermal investigation

A thermogravimetric (TG) measurement was performed between 30 and 500 °C, using a SETARAM TG 92-12 instrument, a nitrogen atmosphere and a heating rate of 5 °C min⁻¹. The sample was kept in an open Al₂O₃ crucible. Differential scanning calorimetry (DSC) was performed using a

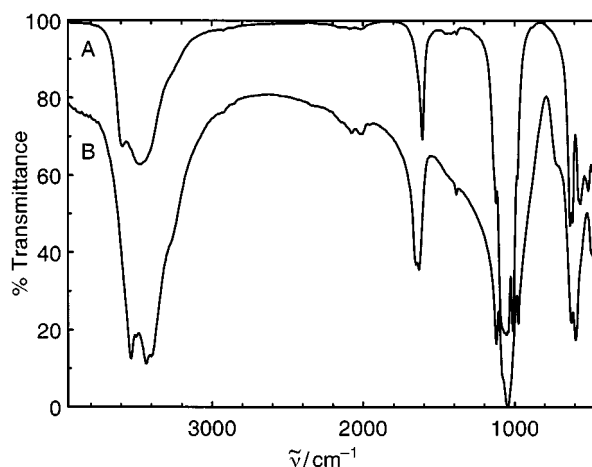


Fig. 3 Infrared spectra of α - (A) and β -LiZnPO₄·H₂O (B)

SETARAM DTA 92-16.18 instrument. The sample was placed in a platinum crucible and α -Al₂O₃ used as reference. The experiment was carried out between 20 and 900 °C using a heating and cooling rate of 5 °C min⁻¹ in an argon atmosphere. Two experiments were carried out using the same sample. The temperature and enthalpy change calibration was carried out using the low-high quartz transition and the dehydration of CaSO₄·2H₂O. Baseline fluctuations in the temperature range 20 to 130 °C are due to small differences between the set temperature and the actual temperature in the DSC instrument.

Results and Discussion

Thermogravimetric measurements were in accordance with the formula β -LiZnPO₄·H₂O, observed weight loss 9.1% at 120–210 °C (calculated 9.7%). The density of β -LiZnPO₄·H₂O was measured using pycnometry and water to *D*_m = 3.01 g cm⁻³, and the calculated density was *D*_c = 2.959 g cm⁻³. The density of α -LiZnPO₄·H₂O is *D*_c = 2.886 g cm⁻³.^{9a}

Phosphorus-31 MAS NMR spectroscopy on β -LiZnPO₄·H₂O showed two signals with chemical shifts δ(³¹P) 6.94(2) and 7.88(2), in accordance with the crystallographic data revealing two phosphorus atoms in the asymmetric unit. The two polymorphs of LiZnPO₄·H₂O thus have distinct phosphorus chemical shifts as α -LiZnPO₄·H₂O shows only one signal [at δ(³¹P) 6.05(2)].^{9b}

Infrared spectra of the two polymorphs of LiZnPO₄·H₂O are illustrated in Fig. 3. The absorptions at ca. 3500 and ca. 1600 cm⁻¹ are due to stretch and bending vibrations in water molecules. A broad absorption in the spectrum of α -LiZnPO₄·H₂O around 3400 cm⁻¹ indicates the presence of adsorbed water, whereas multiple absorptions in the range 3300–3600 cm⁻¹ suggest more than one inequivalent crystal water molecule in β -LiZnPO₄·H₂O. Orthophosphates generally show a strong absorption band in the range 940–1120 and medium at 540–650 cm⁻¹, due to framework vibrations.¹⁹ Differences in this part of the spectra, Fig. 3, suggest differences in the framework structure of the two polymorphs, as will be discussed in the following.

Crystal structure of β -LiZnPO₄·H₂O

The crystal structure of β -LiZnPO₄·H₂O is built from regular tetrahedra of ZnO₄ and PO₄ and slightly distorted tetrahedra of LiO₄. Selected bond lengths and angles are found in Table 3. Chains of alternating ZnO₄ and PO₄ tetrahedra run in the *c* direction. One half the chains have all tetrahedra pointing up (U) and the other chains have tetrahedra pointing down (D). Fig. 4(a) illustrates the connection between two chains forming zigzag four-ring chains parallel to the *c* axis. Fig. 4(b) displays how the double chains of four-ring chains are interconnected to

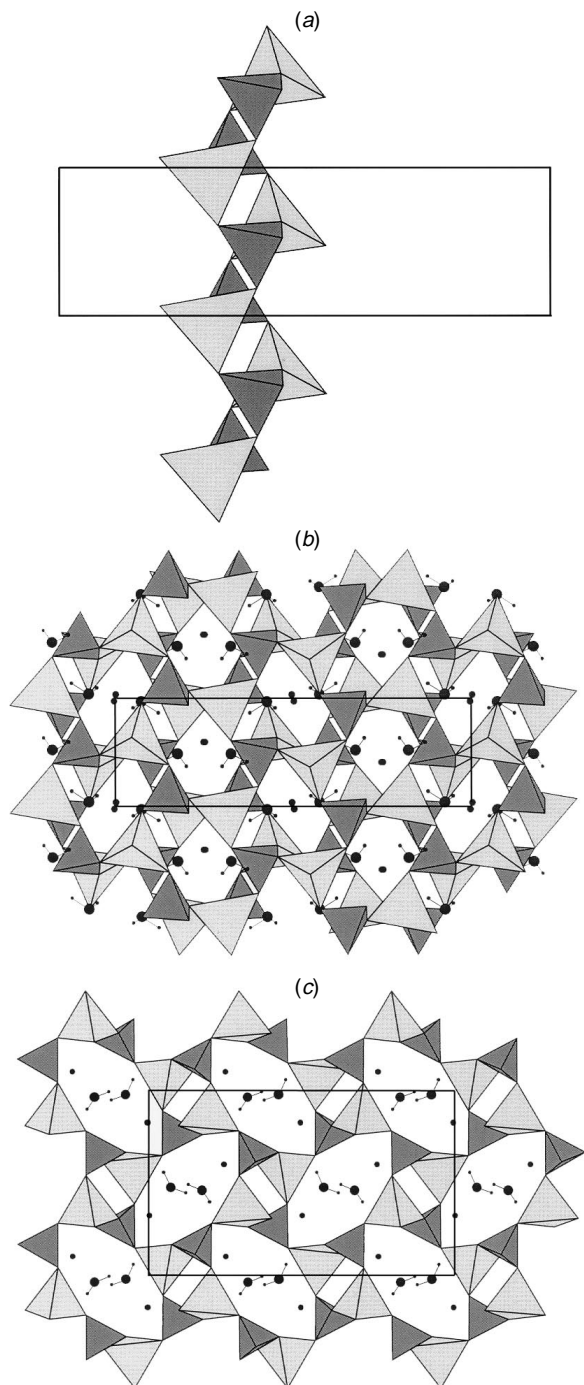


Fig. 4 Crystal structure of β -LiZnPO₄·H₂O: (a) the *b,c* projection, showing four-ring chains in the *c* direction; (b) connectivity of the four-ring chains forming nets of six-ring channels with stacking sequence, ABA, in the (100) direction; (c) the *a,b* projection, showing four- and eight-ring channels in the *c* direction with water and Li atoms placed in the eight rings. The ZnO₄ are grey and PO₄ are dark tetrahedra, lithium ions are shown as medium size black circles and water molecules as small (H atoms) and large (O atoms) black circles

form nets of six rings with the tetrahedra sequence UUDDDD, a characteristic feature of the ABW topology.^{6b,13} Two types of six rings appear trigonally and ovally distorted having the symmetry of twofold axes and *a* glide planes, respectively. The trigonal shape resembles the shape of six rings found in the structures of α -LiZnPO₄·H₂O and tridymite, whereas the oval resembles δ_1 -LiZnPO₄ and cristobalite (the sequence of tetrahedra in a six ring of the three latter compounds are UDUDUD).^{9b,20} The *b,c* projection, Fig. 4(b), consists of pseudo-hexagonal layers stacked with the sequence ABA to

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for β -LiZnPO₄·H₂O; U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor. Parameters for H atoms were not refined

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Zn(1)	1521(1)	6912(1)	4606(2)	10(1)
Zn(2)	9184(1)	5564(1)	1108(2)	10(1)
P(1)	8494(2)	6581(1)	5875(3)	7(1)
P(2)	7232(2)	4082(1)	149(4)	8(1)
Li(1)	9007(17)	7524(8)	923(20)	16(3)
Li(2)	1768(13)	4971(7)	4694(24)	15(3)
O(1)	9584(5)	7041(3)	4330(10)	13(1)
O(2)	1915(5)	5974(3)	6867(9)	13(1)
O(3)	2393(5)	6764(3)	1078(9)	11(1)
O(4)	8326(5)	5740(3)	4615(10)	10(1)
O(5)	1116(5)	5463(3)	1360(10)	12(1)
O(6)	8865(5)	6510(3)	8823(9)	12(1)
O(7)	2181(5)	7953(3)	5676(10)	14(1)
O(8)	8531(5)	4552(3)	9731(10)	12(1)
O(9)	393(6)	8247(3)	9846(11)	22(1)
O(10)	261(6)	4260(4)	5348(11)	23(1)
H(1)	1026	8000	8687	90
H(2)	84	8707	9102	90
H(3)	529	3788	6369	90
H(4)	9428	4500	5914	90

form a three-dimensional framework structure, as illustrated in Fig. 4(c) viewed along the *c* axis, showing another characteristic feature of the ABW topology: four- and eight-ring channels in the (001) direction. The water molecules and lithium ions are placed in the eight-ring channels as shown in Fig. 4(c).

Oxidation states, V_i , were calculated as a sum of bond valences, s , using the equation $s = \exp[(r_0 - r)/B]$, where r_0 and B are empirical parameters [$r_0(\text{P-O}) = 1.617$, $r_0(\text{Zn-O}) = 1.704$, $r_0(\text{Li-O}) = 1.466$, $r_0(\text{H-O}) = 0.882$ and $B = 0.37 \text{ \AA}$] and r is the bond length from the refined structural model.²¹ The calculated oxidation states, V_i , are in Table 4, and the calculated values are in agreement with the expected oxidation states. The values of the oxygen atoms fall in three groups. The framework oxygen atoms co-ordinated to one P, Zn and Li each, O(1)–O(6), have calculated oxidation states, V_i , in the range 1.94–2.01. The framework oxygen atoms co-ordinated to two cations, O(7) and O(8), have lower V_i , 1.83 and 1.81, possibly due to a bond valence contribution from hydrogen bonding. The oxygen atoms in the water molecules, O(9) and O(10), gave values of 2.07 and 1.75, respectively. The low value of O(10) is due to long O(10)–H(3,4) bonds.

Comparison with related zeolite ABW type materials

A variety of different materials adopt the zeolite ABW type structure and crystallise with at least six different space group symmetries.²² A new modification of the ABW structure is adopted by β -LiZnPO₄·H₂O crystallising with space group symmetry $P2_1ab$. The material LiAlSiO₄·H₂O, zeolite LiA(BW), and α -LiZnPO₄·H₂O crystallise in the space group $Pna2_1$, *i.e.* the twofold screw axes are placed inside and parallel to the four-ring chains. The tetrahedra in each four ring are pairwise symmetry related and all tetrahedra point in the same direction viewed along the polar *c* axis in the structure of α - (see Fig. 5) whereas in β -LiZnPO₄·H₂O one half point up and one half down, UUDD [see Fig. 4(c)]. In the structure of β -LiZnPO₄·H₂O the twofold screw axes are in the centre of the six rings, and perpendicular to the four-ring chains, *i.e.* the tetrahedra in a four ring are crystallographically distinct.

The connectivity of the tetrahedra is the same for LiAlSiO₄·H₂O, α -LiZnPO₄·H₂O and β -LiZnPO₄·H₂O; they all have the characteristic ABW topology and as other lithium-containing zeolitic materials they have high framework densities, 19.0, 18.8 and 19.2 T/1000 \AA^3 , respectively.

Table 3 Selected bond lengths (Å) and angles (°) for β -LiZnPO₄·H₂O. Symmetry transformations used to generate equivalent atoms: (i) $x - 1, y, z$; (ii) $x, y, z - 1$; (iii) $x + 1, y, z$; (iv) $x + \frac{1}{2}, -y + \frac{3}{2}, z$; (v) $x + \frac{1}{2}, -y + 1, -z + 1$; (vi) $x + \frac{1}{2}, -y + 1, -z$; (vii) $x + 1, y, z - 1$; (viii) $x - \frac{1}{2}, -y + 1, -z + 1$; (ix) $x - 1, y, z + 1$

Zn(1)–O(7)	1.922(5)	O(7)–Zn(1)–O(1 ⁱ)	105.3(2)
Zn(1)–O(1 ⁱ)	1.958(5)	O(7)–Zn(1)–O(2)	118.6(2)
Zn(1)–O(2)	1.964(5)	O(1 ⁱ)–Zn(1)–O(2)	109.1(2)
Zn(1)–O(3)	1.988(5)	O(7)–Zn(1)–O(3)	102.0(2)
		O(1 ⁱ)–Zn(1)–O(3)	112.7(2)
		O(2)–Zn(1)–O(3)	109.1(2)
Zn(2)–O(8 ⁱⁱ)	1.927(5)	O(8 ⁱⁱ)–Zn(2)–O(5 ⁱⁱⁱ)	106.7(2)
Zn(2)–O(5 ⁱⁱⁱ)	1.948(5)	O(8 ⁱⁱ)–Zn(2)–O(6 ^{iv})	115.4(2)
Zn(2)–O(6 ^{iv})	1.967(5)	O(5)–Zn(2)–O(6 ^{iv})	105.5(2)
Zn(2)–O(4)	1.979(5)	O(8 ⁱⁱ)–Zn(2)–O(4)	107.4(2)
		O(5 ⁱⁱⁱ)–Zn(2)–O(4)	112.8(2)
		O(6 ^{iv})–Zn(2)–O(4)	109.2(2)
P(1)–O(6)	1.528(5)	O(6)–P(1)–O(7 ^v)	108.1(3)
P(1)–O(7 ^v)	1.529(6)	O(6)–P(1)–O(4)	110.8(3)
P(1)–O(4)	1.538(5)	O(7 ^v)–P(1)–O(4)	109.6(3)
P(1)–O(1)	1.541(5)	O(6)–P(1)–O(1)	110.6(3)
		O(7 ^v)–P(1)–O(1)	109.1(3)
		O(4)–P(1)–O(1)	108.7(3)
P(2)–O(2 ^v)	1.532(5)	O(2 ^v)–P(2)–O(8 ⁱⁱ)	109.9(3)
P(2)–O(8 ⁱⁱ)	1.532(5)	O(2 ^v)–P(2)–O(3 ^{vi})	111.0(3)
P(2)–O(3 ^{vi})	1.537(5)	O(8 ⁱⁱ)–P(2)–O(3 ^{vi})	108.6(3)
P(2)–O(5 ^v)	1.546(5)	O(2 ^v)–P(2)–O(5 ^v)	110.9(3)
		O(8 ⁱⁱ)–P(2)–O(5 ^v)	107.5(3)
		O(3 ^{vi})–P(2)–O(5 ^v)	108.9(3)
Li(1)–O(9 ^{vii})	1.91(2)	O(9 ^{vii})–Li(1)–O(1)	106.6(8)
Li(1)–O(1)	1.972(12)	O(9 ^{vii})–Li(1)–O(6 ^{iv})	115.6(7)
Li(1)–O(6 ^{iv})	1.987(13)	O(1)–Li(1)–O(6 ^{iv})	97.9(6)
Li(1)–O(3 ^{iv})	2.00(2)	O(9 ^{vii})–Li(1)–O(3 ^{iv})	103.3(6)
		O(1)–Li(1)–O(3 ^{iv})	116.2(6)
		O(6 ^{iv})–Li(1)–O(3 ^{iv})	117.4(8)
Li(2)–O(10)	1.943(14)	O(10)–Li(2)–O(5)	97.8(6)
Li(2)–O(5)	1.971(13)	O(10)–Li(2)–O(2)	118.0(6)
Li(2)–O(2)	1.992(13)	O(5)–Li(2)–O(2)	98.2(6)
Li(2)–O(4 ^{viii})	1.985(13)	O(10)–Li(2)–O(4 ^{viii})	102.9(6)
		O(5)–Li(2)–O(4 ^{viii})	130.8(6)
		O(2)–Li(2)–O(4 ^{viii})	109.9(6)
O(9)–H(1)	0.952(5)	Li(1 ^{ix})–O(9)–H(1)	112.8(6)
O(9)–H(2)	0.904(6)	Li(1 ^{ix})–O(9)–H(2)	113.3(7)
O(10)–H(3)	0.972(6)	H(1)–O(9)–H(2)	109.8(5)
O(10)–H(4)	1.018(6)	Li(2)–O(10)–H(3)	111.2(6)
		Li(2)–O(10)–H(4)	84.3(6)
		H(3)–O(10)–H(4)	159.4(7)

Synthesis

In a previous study α -LiZnPO₄·H₂O was found to crystallise from the system LiOH–Zn(NO₃)₂–H₃PO₄–water.⁴ Hydrothermal syntheses from the system LiOH–Zn(CH₃CO₂)₂–H₃PO₄–water suggest that α -LiZnPO₄·H₂O is in fact a metastable intermediate phase that transforms to β -LiZnPO₄·H₂O, *i.e.* the system approaches higher density and higher thermodynamic stability: gel \rightarrow α -LiZnPO₄·H₂O \rightarrow β -LiZnPO₄·H₂O. The material α -LiZnPO₄·H₂O has only been obtained as a microcrystalline powder, whereas β -LiZnPO₄·H₂O can be obtained as larger crystals. This is probably due to the very different timescales of nucleation and crystal growth for α - and β -LiZnPO₄·H₂O.

Thermal investigation

Phase transformations of α - and β -LiZnPO₄·H₂O were investigated by hydrothermal and dry heating. Hydrothermal heating of α -LiZnPO₄·H₂O at ultra high pressure (80 °C, 10 kbar, 20 h) produced β -LiZnPO₄·H₂O, *i.e.* approaching higher density. Fig.

Table 4 Calculated oxidation states, V_i , for the structure of β -LiZnPO₄·H₂O, using ref. 21

Cation	No.	V_i	Co-ordination number	
Phosphorus	1	5.01	4	
	2	4.97	4	
Zinc	1	2.02	4	
	2	2.03	4	
Lithium	1	1.04	4	
	2	1.02	4	
Oxygen Framework	1	1.99	3	
	2	2.00	3	
	3	1.94	3	
	4	1.96	3	
	5	1.98	3	
	6	2.01	3	
	7	1.83	2	
	8	1.81	2	
	Water	9	2.07	3
		10	1.75	3

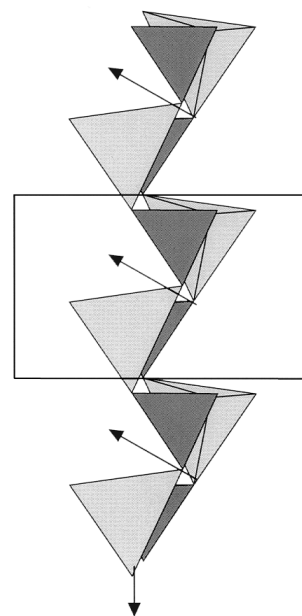


Fig. 5 Crystal structure of α -LiZnPO₄·H₂O, the b,c projection showing four-ring chains in the c direction. The arrows indicate a mechanism for a displacive phase transition of α - to β -LiZnPO₄·H₂O, *i.e.* the tetrahedra in the lower chain are rotated by *ca.* 45° and the upper chain is moved slightly downwards. The ZnO₄ are shown as grey and PO₄ as dark tetrahedra

5 shows the b,c projection of α -LiZnPO₄·H₂O with four-ring chains in the c direction and arrows indicate how α - transforms into β -LiZnPO₄·H₂O by a displacive phase transition [compare Fig. 5 and 4(a)]. Half the chains of tetrahedra (the lower chain in Fig. 5) are distorted as indicated by the arrows, *i.e.* the tetrahedra are rotated by *ca.* 45°. The tetrahedra in the upper chain are all moved slightly. The mean angle between the framework tetrahedral atoms, T–O–T angles, in α - and β -LiZnPO₄·H₂O are similar, 125.2 and 128.3°, respectively.

Hydrothermal heating of α -LiZnPO₄·H₂O at $T > 100$ °C was found to produce δ_1 -LiZnPO₄,⁹ and the mechanism appeared to be solution mediated.²³ The compound β -LiZnPO₄·H₂O also transforms into δ_1 -LiZnPO₄ upon hydrothermal treatment at >100 °C. The dry heating dehydration of β -LiZnPO₄·H₂O was investigated using differential scanning calorimetry giving an enthalpy change of $\Delta H = 43(6)$ kJ mol⁻¹, peak value at 219(2) °C, for the irreversible phase transformation of β -LiZn-

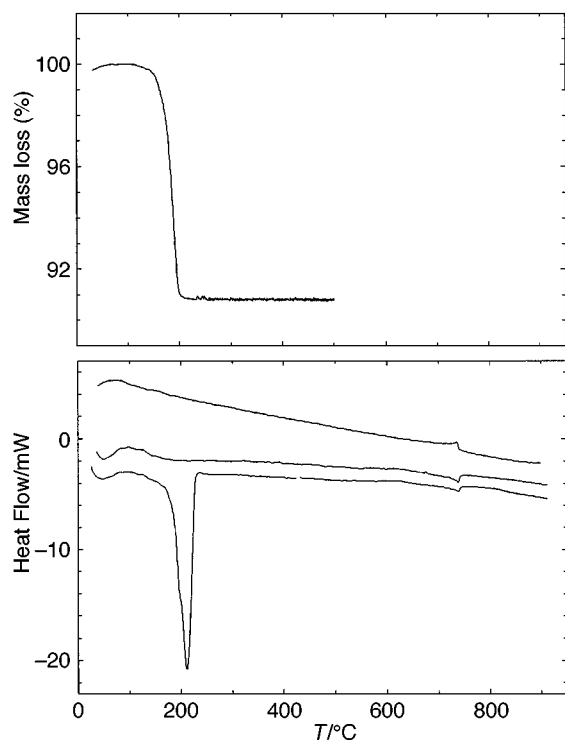


Fig. 6 Thermal investigation of β -LiZnPO₄·H₂O showing the mass loss detected by thermogravimetry (upper graph) and differential scanning calorimetry; the lower and the middle DSC curves are the first and second heating and the upper DSC curve is one of the very similar cooling curves

PO₄·H₂O into δ -LiZnPO₄. A shoulder, at ca. 206 °C, was found on the DSC signal for the dehydration, Fig. 6, but the TG trace suggests a one-step process. A weak signal at 738(1) °C shows the phase transition of δ -LiZnPO₄ into β -LiZnPO₄ in accordance with the equilibrium phase diagram.¹¹ The DSC trace resembles a shift in baseline indicating that mainly a change in heat capacity is taking place. Cooling β -LiZnPO₄ produces α -LiZnPO₄ [$a = 17.240(2)$, $b = 9.768(1)$, $c = 17.106(1)$ Å and $\beta = 110.90(1)^\circ$, refined from powder diffraction data, 118 reflections] and the α - to β -LiZnPO₄ phase transition is shown to be reversible in Fig. 6.

The zeolites MAISiO₄· x H₂O ($M = \text{Li, Na or Ag}$) show a large framework flexibility as the dehydrated polymorphs may retain the ABW topology and the aluminosilicates of Na and Ag have partly dehydrated ABW polymorphs ($x = 0.8$ and $x = 0.8$ and 0.68 , respectively).²⁴ Further heating of the dehydrated ABW type LiAlSiO₄ produces a stuffed cristobalite-type structure,^{24b} which is similar to the phase transition of α - and β -LiZnPO₄·H₂O to δ -LiZnPO₄.

Conclusion

Investigation of the system LiOH–Zn(CH₃CO₂)₂–H₃PO₄–water, revealed that a new phase of LiZnPO₄·H₂O can be prepared under ambient conditions. A known polymorph of LiZnPO₄·H₂O (ABW structure, space group $Pna2_1$) was found as an intermediate phase during the synthesis and transforms into β -LiZnPO₄·H₂O by hydrothermal heating at ultra high pressure. A mechanism for the displacive phase transition is proposed. Hydrothermal or dry heating of β -LiZnPO₄·H₂O at >100 °C produces δ -LiZnPO₄. The crystal structure of β -LiZnPO₄·H₂O can be viewed as framework structures built from PO₄ and ZnO₄ tetrahedra with LiO₄ tetrahedra and water molecules placed in eight-ring channels running in the c direction. This compound is apparently the only member of the zeolite ABW group of materials crystallising in space group $P2_1ab$.

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