

A novel layered templated lithium zinc phosphate prepared by an unusual solution mediated technique

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Received (in Bristol, UK) 11th November 1998, Accepted 12th January 1999

A novel layered lithium zinc phosphate $\text{LiZn}(\text{HPO}_4)(\text{PO}_4)\cdot\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3\cdot\text{H}_2\text{O}$ containing ethylenediamine(en), having a long nucleation time, is prepared by moderate temperature solution mediated conversion of a microporous zinc phosphate; its crystal structure is also reported.

Synthetic microporous and layered materials are of considerable interest for a wide variety of industrial and chemical applications, e.g. catalysis, ion exchange or intercalation.¹ These materials have expanded their range of compositions tremendously from the original zeolite type aluminium silicate minerals and now include phosphates, arsenates, vanadates, and chalcogenides.² Orthophosphates are possibly the fastest expanding group of inorganic materials and recently templated iron phosphates were discovered, arising from the development of new solvothermal synthesis techniques.³

Solvothermal synthesis using organic amine ions as templates is a common route to novel open framework materials and detailed knowledge of the synthesis mechanism, including nucleation and crystal growth, is of importance for the design of new materials.⁴ The formation of a Mn substituted aluminium phosphate (Mn-AIPO-5, AFI structure) was investigated using *in situ* synchrotron radiation powder diffraction. The crystal growth followed a first order kinetic model after a nucleation period; clearly, lowering the synthesis temperature increases the nucleation time.⁵ Similar main features were found for the crystallisation of a microporous oxyfluorinated gallophosphate, ULM-5.⁶ Changing the composition of reactants for the ULM-5 synthesis revealed the presence of an intermediate phase; decreasing the synthesis temperature increases the time of stability of the intermediate.⁶ In general microporous and layered materials are topologically metastable and convert to more dense phases upon heating dry or in water, i.e. approaching higher density and higher thermodynamic stability. In some cases microporous materials can transform to other microporous or layered materials upon prolonged solvothermal treatment at a constant moderate temperature. The materials prepared by such solution mediated conversion might not be attainable increasing the synthesis temperature as the system enters the stability field of other more dense phases. β - $\text{LiZnPO}_4\cdot\text{H}_2\text{O}$, a new variant of the zeolite ABW structure, was initially prepared at room temperature by solution mediated conversion of α - $\text{LiZnPO}_4\cdot\text{H}_2\text{O}$ having a nucleation period of ca. 3 months.⁷ Variation of the composition of the reaction mixture revealed that β - $\text{LiZnPO}_4\cdot\text{H}_2\text{O}$ could be prepared with a nucleation period of several days.⁷ Ambient temperature solution mediated conversion of one metastable phase to another is probably useful in a wide range of chemical compositions for discovering new materials and the method might be characterised as a *chemie douche* technique.⁸ Another approach utilises slow diffusion of the reactants in a silica gel. After a nucleation period of ca. 3 weeks at ambient conditions crystals of new layered templated aluminium and gallium phosphates appeared.⁹

The method of solution mediated conversion is utilised in the present study preparing zinc hydrogenphosphates containing rubidium or caesium and a new layered templated lithium zinc

phosphate $\text{LiZn}(\text{HPO}_4)(\text{PO}_4)\cdot\text{H}_2\text{en}\cdot\text{H}_2\text{O}$ **1**; all the materials have long nucleation time.

We have discovered a new rubidium zinc hydrogenphosphate, $\text{Rb}_2\text{Zn}_2(\text{HPO}_4)_3$ prepared at 51 °C with nucleation time of ca. 4.5 months [monoclinic, space group $P2_1/c$, $a = 12.5880(4)$, $b = 12.7170(8)$, $c = 7.5827(8)$ Å, $\beta = 96.100(1)^\circ$]. This material has a complex crystal structure with spiralling chains of ZnO_4 and HPO_4 tetrahedra.¹⁰ At ambient conditions we also prepared a new layered caesium zinc hydrogenphosphate, $\text{CsZn}_{2.5}(\text{HPO}_4)_3\cdot 2\text{H}_2\text{O}$, by a solution mediated conversion after a nucleation period of ca. 2 months [triclinic, space group $P1$, $a = 8.3918(6)$, $b = 9.8254(8)$, $c = 9.9090(7)$ Å, $\alpha = 111.17(1)$, $\beta = 111.75(1)$, $\gamma = 97.56(1)^\circ$].¹¹

The synthesis of **1** was performed in the system $\text{Li}/\text{Zn}/\text{PO}_4\text{-en}\cdot\text{H}_2\text{O}$; a gel was left to stand at 21 °C in a sealed flask preventing evaporation.[‡] After 1 day a microporous zinc phosphate, $\text{Zn}_2(\text{PO}_4)_2\cdot\text{H}_2\text{en}$, DAF-3,¹² formed and after ca. 3 months crystallisation of **1** was observed thus, DAF-3 is a metastable, intermediate phase. The material DAF-3 has only been obtained as microcrystalline powder, whereas **1** can be obtained as larger crystals. This is probably due to very different time-scales of nucleation and crystal growth for the two materials. A faster and more direct preparative route for **1** might exist but not at much higher temperatures owing to formation of more dense phases, e.g. δ_1 - LiZnPO_4 .¹³

The crystal structure of **1** was investigated by single crystal X-ray diffraction providing a detailed structural model including all hydrogen positions in space group $C2/c$. **1** is built from regular tetrahedra of PO_4 , ZnO_4 and LiO_4 forming two types of chains running in the (010) direction; zigzag four ring chains of alternating PO_4 and ZnO_4 and chains of corner sharing LiO_4 , each LiO_4 tetrahedron having one oxygen from crystal water. These chains are alternately connected by HPO_4 tetrahedra forming layers held together by hydrogen bonding through ethylenediamine and water. Fig. 1 shows the *ac* projection of the crystal structure of **1**. Half the H_2en ions were found across a symmetry centre and are connecting the zigzag chains. The other H_2en ions connecting LiO_4 chains in different sheets are placed across the twofold axes of the space group $C2/c$ in such a way that the individual H_2en ions do not obey this symmetry, necessitating a disordered structural model in $C2/c$ or lowering the symmetry to Cc . The refinement in Cc was unstable unless all except this dication was constrained to keep the centrosymmetric relation. In fact the least squares program, KRYSTAL,¹⁴ has been modified to allow symmetry operations which apply to a specified number of atoms only. The two models have the same number of parameters and gave similar *R*-values. We therefore chose the $C2/c$ solution.

1 is the first layered material in the system $\text{M}_2\text{O}-\text{ZnO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}-\text{amine}$, $\text{M} = \text{alkali metal}$, with only one other member, reported as $\text{Na}_{67}(\text{NMe}_4)_{12}\text{Zn}_8(\text{ZnPO}_4)_{96}\cdot 192\text{H}_2\text{O}$, an analogue to zeolite X.¹⁵ The latter is partly templated by hydrated sodium ions and partly by the amine ions. A large number of alkali metal containing microporous and some layered materials have been described, e.g. two ABW type polymorphs of $\text{LiZnPO}_4\cdot\text{H}_2\text{O}$ denoted α and β ,^{7,13a} but **1** is the first compound with alkali metal–oxygen–alkali metal contact, although $\text{Zn}-\text{O}-\text{Zn}$ linkages are known, but rare.¹⁶ Fig. 2 shows the connectivity of

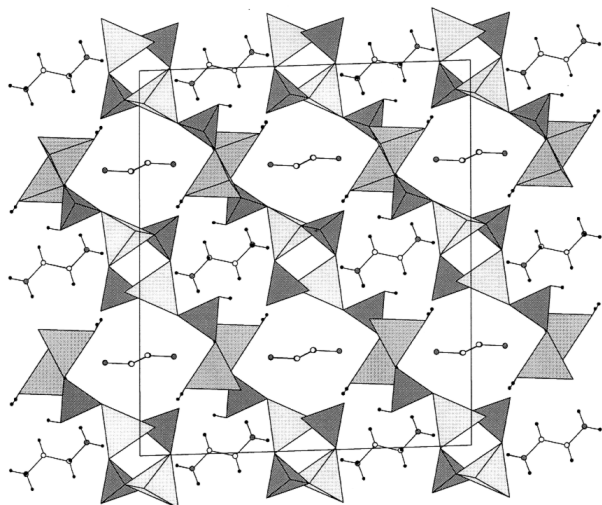


Fig. 1 The crystal structure of **1**; the *ac* projection. PO₄ (dark) and ZnO₄ (light) tetrahedra forming four-ring chains along with LiO₄ (medium dark) chains are running in the (010) direction, connected by HPO₄ tetrahedra to form layers, which are assembled by linking ethylenediamine ions. H atoms small size dark circles, C and N atoms larger medium dark circles.

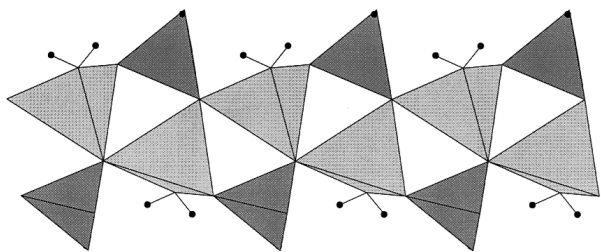


Fig. 2 The Li–O–Li chains running along the *b* axis in the crystal structure of **1**. Hydroxyl hydrogen and H atoms in the water molecules coordinated to Li shown as small size dark circles, PO₄ dark and LiO₄ medium dark tetrahedra.

the Li–O–Li chains in the crystal structure of **1**. These chains are similar to the Zn–O–Zn chains in a newly reported H₂en containing zinc phosphate, Zn₆(HPO₄)(PO₄)₄·H₂en·H₂O.^{16b} The material **1** has a rare layered crystal structure assembled by linking amine ions.

A Danish Technical Research Council PhD grant is gratefully acknowledged. The Siemens SMART diffractometer at Chemistry Department, Aarhus University was partly financed by Carlsbergfondet.

Notes and references

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‡ *Synthesis*: LiZn(HPO₄)(PO₄)·H₂en·H₂O **1** was prepared by dissolving LiOH·H₂O (1.833 g), LiCl (1.867 g) and Zn(MeCO₂)₂·2H₂O (9.639 g) in water. H₃PO₄ 85% (10.022 g) and then ethylenediamine (en) (4.6 mL) were added under stirring forming a white gel with composition, 0.99 Li₂O : 1 ZnO : 0.98 P₂O₅ : 1.92 en : 43 H₂O, *c*(PO₄) *ca.* 1.7 M, pH = 4.95. A portion of this gel was left to stand at ambient conditions, *ca.* 21 °C, in a sealed bottle preventing evaporation. After *ca.* 24 h DAF-3 was formed as a microcrystalline powder [*a* = *b* = 14.7073(8), *c* = 8.946(1) Å, refined from 103 powder diffraction reflections, in accordance with ref. 12] and after *ca.* 3 months DAF-3 partly transformed to **1**.

§ *Single crystal diffraction*: A transparent, plate-like crystal of **1** was selected for data collection on a Siemens SMART diffractometer equipped with a CCD detector and graphite monochromatised Mo-K α radiation, λ =

0.71073 Å. Approximately one hemisphere of data was collected in narrow 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 an empirical method (SADABS) giving 1616 unique reflections.

Details of data collection: θ_{\max} = 24.5°, *T* = 120(2) K, measured reflections 4108, *R*_{int} = 0.027, Transmission (max. min.): 0.93, 0.80. A structural model was found using direct methods and the program SIR97.¹⁷ The program KRYSTAL was used for the structure refinement.¹⁴ The H atom positions were found in the difference Fourier maps and thermal parameters were kept isotropic; all other atoms were refined with anisotropic temperature factors. Scattering factors of neutral atoms were applied throughout this work. The refinement converged at *R* = 0.027 and *R*_w = 0.035, with 183 parameters refined using full matrix least squares based on *F*² and a weighting scheme, $w = \{[\sigma_{cs}(F^2) + 0.03F^2]^{-2}\}$. Figures were prepared using the program Atoms Ver. 4.0.¹⁸

Crystal data for 1: *M* = 343.41, monoclinic, space group *C2/c*, (no. 15), *a* = 18.068(2), *b* = 5.3034(6), *c* = 21.065(3) Å, β = 91.992(2)°, *U* = 2017.3(4) Å³, *Z* = 8, μ = 2.794 mm⁻¹, *D*_c = 2.261 g cm⁻³. CCDC 182/1146. See <http://www.rsc.org/suppdata/cc/1999/371/> for crystallographic files in .cif format.

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Communication 8/092721