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Direct *in situ* observation of increasing structural dimensionality during the hydrothermal formation of open-framework zinc phosphates

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The first time-resolved *in situ* X-ray diffraction studies of the hydrothermal crystallisation of open-framework zinc phosphates reveal a pathway of sequential crystallisation involving formation of a metastable low dimensional chain phase before the growth of three-dimensional zeolitic architectures.

A great deal of effort is currently focussed on understanding the crystallisation mechanism of microporous solids which can have applications in shape-selective catalysis, separation science, and ion-exchange. It is hoped that an understanding of mechanisms leading to the formation of these zeolite-like solids at the atomic-scale will allow the rational synthesis of new materials.^{1,2} The common use of hydrothermal synthesis conditions in the preparation of such open-framework solids requires sealed thick-walled reaction vessels and it is only in recent years that *in situ* probes of hydrothermal crystallisation have been developed to follow reactions under these experimentally-challenging conditions.³ For example, in a study of the phosphates of gallium using energy-dispersive X-ray diffraction (EDXRD) some of us have observed previously-unknown, transient phases prior to the onset of crystallisation of open-framework phases,^{4,5} and Taulelle *et al.* have identified oligomeric 'building blocks' in hydrothermal reaction solutions using NMR spectroscopy.⁶ The results of such studies provide a foundation on which to build descriptions of reaction mechanisms.

The first results of an *in situ* EDXRD study of the hydrothermal synthesis of zinc phosphates are described here. This large family of solids has recently been the focus of study by some of us, and an Aufbau principle for the building up of three-dimensional structures from structures of lower dimensionalities proposed.⁷ With an aim of gaining further information about crystallisation mechanisms it is crucial to study systems such as these using *in situ* measurements of crystallisation, since it has been established that on arresting a hydrothermal reaction by cooling to room temperature the material recovered is not necessarily representative of the material present under reaction conditions.^{4,5} The EDXRD method uses intense synchrotron X-rays which allows the use of a laboratory-sized hydrothermal reaction vessel, mimicking the conditions employed in the synthetic laboratory and permitting rapid data collection (< 1 min) for kinetic studies. An apparatus developed over the past few years by O'Hare and co-workers⁸ was used in the current work.[†]

In the first zinc phosphate system studied we focussed on the reaction between piperazine phosphate ($[\text{C}_4\text{N}_2\text{H}_{12}][\text{HPO}_4]\cdot\text{H}_2\text{O}$, PIP-P) and zinc oxide in dilute hydrochloric acid solution. Fig. 1 shows a stack plot of the time-resolved EDXRD data measured as a reaction mixture of composition ZnO:1.5 HCl:1.75 PIP-P:100 H₂O which was heated to 180 °C in an

autoclave at *ca.* 5 °C min⁻¹ (detector angle 0.9325°). The use of a three-element energy discriminating detector system⁹ allows unambiguous identification of known crystalline phases, owing to the large amount of diffraction data that can be simultaneously recorded.¹⁰ Characteristic Bragg reflections of the phosphate and amine source, PIP-P, are observed only during the first minute before disappearing; presumably this is due to dissolution of this rather soluble species. Remarkably, we observe that characteristic Bragg reflections of a known zinc phosphate, $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}(\text{HPO}_4)_2(\text{H}_2\text{O})]$ (ZnPO-PIP-I),¹¹ are present in the first spectrum recorded (31 °C), suggesting that this material forms on mixing the chemicals at room temperature. The compound has a 1-D ladder structure (see Table 1 for descriptions of the phases discussed in this paper). After heating to 163 °C new strong Bragg reflections (of a phase not yet identified) are apparent, and these diffraction features, along with those of ZnPO-PIP-I, have constant intensity for 30 min during which time a temperature of 180 °C is reached. Over a period of 10 min, these two phases and the starting material ZnO are replaced by two known zinc phosphates, $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}_{3.5}(\text{PO}_4)_3(\text{H}_2\text{O})]$ (ZnPO-PIP-II)^{11,12} and $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}_2(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_2]$ (ZnPO-PIP-III),¹¹ which are the sole two products after 145 min of heating. ZnPO-PIP-II and ZnPO-PIP-III both have three-dimensional framework structures.

On changing the amount of PIP-P we observed rather different behaviour. For a mixture of composition ZnO:1.5 HCl:1 PIP-P:100 H₂O, held at a constant temperature of 180 °C, the ladder phase ZnPO-PIP-I is present in the first spectrum

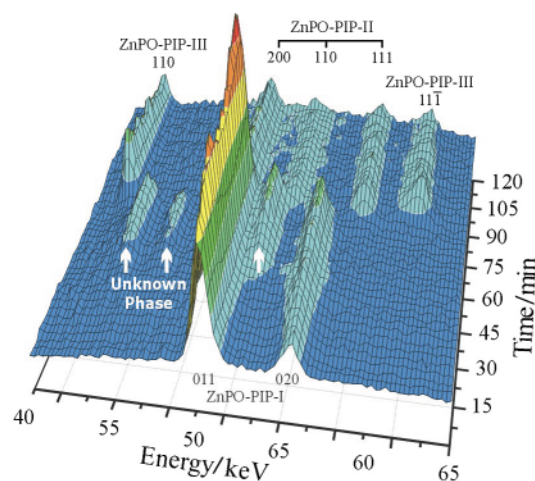


Fig. 1 A stack plot of EDXRD data measured during the sequential crystallisation of zinc phosphates from the reaction mixture ZnO:1.5 HCl:1.75 PIP-P:100 H₂O.

Table 1 Zinc phosphates observed *in situ* in the ZnO/PIP-P/HCl (aq) system

Compound (dimensionality)	Formula	Miller index, observed <i>d</i> (expected) ^c /Å Lowest EDXRD detector at 0.9325°
ZnPO-PIP-I ^a (1-D)	[C ₄ N ₂ H ₁₂][Zn(HPO ₄) ₂ (H ₂ O)]	011, 7.77 (7.733) 020, 7.05 (7.012)
ZnPO-PIP-II ^{a,b} (3-D)	[C ₄ N ₂ H ₁₂][Zn _{3,5} (PO ₄) ₃ (H ₂ O)]	200, 7.82 (7.813) 110, 7.30 (7.300) 111, 6.74 (6.717)
ZnPO-PIP-III ^a (3-D)	[C ₄ N ₂ H ₁₂][Zn ₂ (HPO ₄) ₂ (H ₂ PO ₄) ₂]	110, 9.285 (9.272) 111, 6.37 (6.325)
ZnPO-PIP-IV ^a (3-D)	[C ₄ N ₂ H ₁₂][Zn(H ₂ O)Zn(HPO ₄)(PO ₄) ₂]	110, 9.35 (9.327) 111, 7.73 (7.703) 020, 7.47 (7.444) 111, 6.99 (6.954) 200, 5.96 (5.983)

^a Ref. 11 ^b Ref. 12. ^c Bottom EDXRD detection.

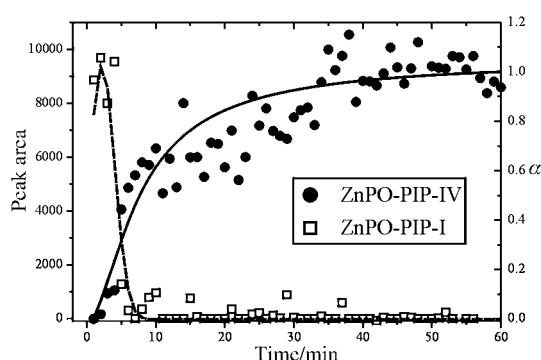


Fig. 2 Integrated peak intensities of ZnPO-PIP-I and ZnPO-PIP-IV during crystallisation from the reaction mixture ZnO : 1.5 HCl : 1 PIP-P : 100 H₂O at 180 °C.

recorded, and almost immediately its Bragg reflections begin to decay. The ladder phase is consequently replaced by a known zinc phosphate with a three-dimensional structure, [C₄N₂H₁₂][Zn(H₂O)Zn(HPO₄)(PO₄)] (ZnPO-PIP-IV).¹¹ The decay of the precursor phase and growth of the product are not mirrored precisely: integrated peak intensities show that an appreciable amount of ZnPO-PIP-I is consumed before ZnPO-PIP-IV is observed. The decay and growth curves cross at $\alpha \approx 0.3$ of product (α is the extent of reaction; see Fig. 2). This suggests that the transformation of the chain material to the three-dimensional structure is a solution-mediated process involving dissolution of the first phase, rather than a solid-state transformation.

We have presented preliminary results of an *in situ* study of the formation of a large family of open-framework materials. The dissolution of starting materials and sequential crystallisation of a number of open-framework solids was directly observed. In certain cases, crystalline materials with as-yet unknown structures form during the reactions. Given the huge number of zinc phosphate structures that can be formed from reaction mixtures of only slightly differing composition, it is not unexpected to discover new metastable phases. The importance of these crystallisation studies is that for the first time we have observed *under real reaction conditions* the sequential crystallisation of materials with increasing dimensionality. Recently it has been shown that a ladder zinc phosphate, similar to that observed as a transient phase in our *in situ* studies, can be used

as a solid precursor to a number of other layered and 3-D phases.¹³ Combined with our *in situ* results, such studies of the reactivity of the ZnPO phases provide convincing evidence for the Aufbau principle proposed recently for the building up of 3-D zinc phosphate structures.⁷ We are currently extending our *in situ* studies to survey other ZnPO/amine systems in order to understand more fully the nature of the structural transformations taking place.

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Notes and references

[†] EDXRD experiments were performed on Station 16.4 of the Daresbury Synchrotron Radiation Source ($I \sim 200$ mA, ~ 2 GeV synchrotron). Station 16.4 was illuminated with X-rays in the energy range 5–120 keV from a 6 T superconducting wiggler insertion device. Diffracted X-rays were measured using a three-element germanium solid-state detector; this allowed access to three *d*-spacing ranges, dependant on the angle to which the detector was set. The delay between mixing reagents, sealing in the hydrothermal autoclave and beginning data collection was of the order of 5 min.

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