Combinatorial approach for the hydrothermal syntheses of open-framework zinc phosphates

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Applying a combinatorial strategy, new zinc phosphates with interesting framework architectures have been hydrothermally synthesized and their structures solved by single-crystal X-ray diffraction analysis.

In recent years combinatorial approaches for the discovery of new materials have attracted considerable attention because of their high efficiency.[1–3] Originating from the discovery of new drugs by pharmaceutical companies, combinatorial methods have been employed in the areas of organic, biochemical and inorganic chemistry.[4–6] The application of combinatorial approaches to hydrothermal synthesis is full of challenges. So far, there are only a few reports on hydrothermal combinatorial synthesis.[7–10] Akporiaye and co-workers first reported the application of a combinatorial strategy to the hydrothermal synthesis of zeolites, which demonstrates the potential strengths of combinatorial approaches in the synthesis of microporous and related materials.[7] Maier *et al.*[8] and Bein *et al.*[9] subsequently developed the methodology based on automatic dispensing of the reagents and identifying the products, respectively. Here we describe the combinatorial approaches for the hydrothermal syntheses of new zinc phosphates using *N,N′*-dimethylpiperazine as a structure-directing agent. The experimental design includes variation of the components of $Zn(OAc)_2$, H_3PO_4 and *N,N′*-dimethylpiperazine, as well as a study of the influence of some transition metal cations on the crystallization. New zinc phosphates have been prepared with interesting framework architectures and in particular, compound **A** exhibits large 16-membered ring channels intersected by 10- and 8-membered channels, which is rare in the family of zinc phosphates.[11–15] Our combinatorial method allows automatic dispensing and mixing of the reagents, as well as automatic separation and identification of the products. This work further demonstrates the potential applications of hydrothermal combinatorial methods to the discovery of new open-framework materials.

Our multiautoclave consists of a stainless steel block with 64 Teflon chambers (0.7 cm in diameter, 3.0 cm in depth, 800 μl in volume per chamber). The reactions were performed in $Zn(OAc)_2$–H_3PO_4–*N,N′*-dimethylpiperazine–H_2O system. $Zn(OAc)_2$ aqueous solution was first added to each individual Teflon chamber using a Tecan CH Miniprep 75 pipette robot, followed by addition of *N,N′*-dimethylpiperazine and H_3PO_4 (85%). The reaction mixtures were shaken for 2 h for homogenization. The multiautoclave was placed in an oven for 60 h at 180 °C. The yield is normally enough for automatic powder XRD analysis, compositional and TG analysis, as well as single-crystal X-ray diffraction determination. The arrays of Teflon chambers were put into a Hermle 2300 centrifuge apparatus for sample separation. The dried samples were transferred to a sample holder for X-ray analysis. Automated X-ray diffraction analysis was carried out with a computer-controlled xyz stage GADDS microdiffractomer from Bruker D8 Discover with a CCD detector using Cu-Kα radiation. Suitable single crystals were selected for single-crystal X-ray diffraction analysis performed on a Siemens diffractometer fitted with a Bruker SMART CCD detector.

In this study, we have investigated the influence of variation of the contents of reagents on the product in the reaction system 1.0 $Zn(OAc)_2$–*x* H_3PO_4–*y* *N,N′*-dimethylpiperazine (R) with a fixed water volume of 0.5 mL for each crystallization. Fig. 1 shows the crystallization fields for two zinc phosphate phases, *i.e.*, a new phase **A** ($[Zn_6P_5O_{20}(H_2O)]\cdot 0.5C_6H_{16}N_2\cdot C_5H_{14}N_2\cdot 3H_2O$), and a known phase **B** ($Zn_3(PO_4)_2H_2O$).[16] It can be seen clearly that phase **A** forms in the range of $0.5 \leqslant P/Zn \leqslant 4$ and $2 \leqslant R/Zn \leqslant 6$ with pH values of 7–9. While increasing the content of H_3PO_4 or decreasing the content of organic amine, *i.e.* decreasing the pH value of the reaction system to 5–7, phase **B** forms in the areas of $0.5 \leqslant P/Zn \leqslant 4$ and $0.33 \leqslant R/Zn \leqslant 1.67$, and $6 \leqslant P/Zn \leqslant 7$ and $3 \leqslant R/Zn \leqslant 6$, respectively. Further decreasing the pH value of the reaction system, the reaction mixtures keep as a clear solution, and no crystalline products are obtained in the range of $5 \leqslant P/Zn \leqslant 7$ and $0 \leqslant R/Zn \leqslant 2$.

We further investigated some transition metal cations such as Co^{2+}, Fe^{2+}, Ni^{2+}, Mn^{2+}, *etc.* on the influence of the crystallization of phase **A** and **B** employing a combinatorial approach. It was found that the existence of Co^{2+} greatly affects the crystallization of phase **A**. Adding Co^{2+} cations to the crystallization field of phase **A** with the Co/Zn molar ratio in the range of 0.2–0.4 causes the formation of a new phase **C** ($[Zn_5P_4O_{16}(H_2O)]\cdot C_4H_{14}N_2$). A small amount of transition metal cations does not affect the crystallization results, whereas when the M^{2+}/Zn molar ratio is above 0.4, the products are amorphous. Inductively coupled plasma (ICP) analysis indicates that Co atoms are not incorporated in phase **C**, suggesting that Co cations play an important role in inducing the nucleation of phase **C**.

Compound **A** ($[Zn_6P_5O_{20}(H_2O)]\cdot 0.5C_6H_{16}N_2\cdot C_5H_{14}N_2\cdot 3H_2O$)† exhibits a novel three-dimensional framework incorporating diprotonated *N,N′*-dimethylpiperazine and *N*-methylpiperazine molecules within the pores. *N*-Methylpiperazine molecules are believed to be decomposed from the *N,N′*-dimethylpiperazine molecules in the reaction mixture under hydrothermal conditions. Its structure consists of ZnO_4, $ZnO_3(H_2O)$ and PO_4 tetrahedra linked through their vertices forming 16-membered channels along the [100] direction,
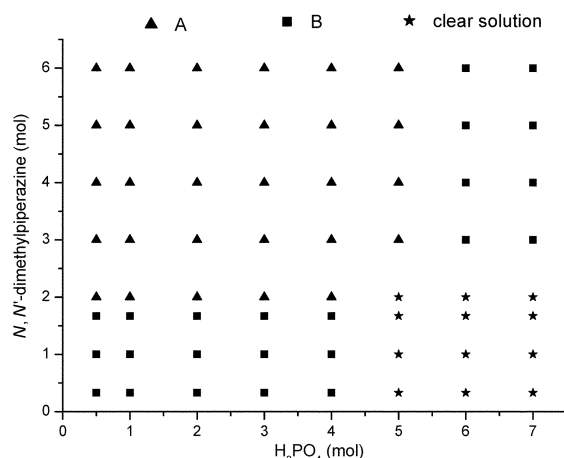

Fig. 1 The crystallization fields of phases **A** and **B**.

which are intersected with 10- and 8-membered ring channels along the [010] and [001] direction, respectively. There are Zn–O–Zn bonds connected through μ_3-O atoms. Fig. 2 shows the framework structure of **A** viewed along the [100] direction. Two diprotonated *N*-methylpiperazine molecules are accommodated in the 16-membered ring channel, while one diprotonated *N,N'*-dimethylpiperazine molecule resides in the 10-membered ring channel. Compound **A** exhibits a unique large channel structure, which is quite rare in open-framework solids and there are only a few such reports in open-framework zinc phosphates.[17–21]
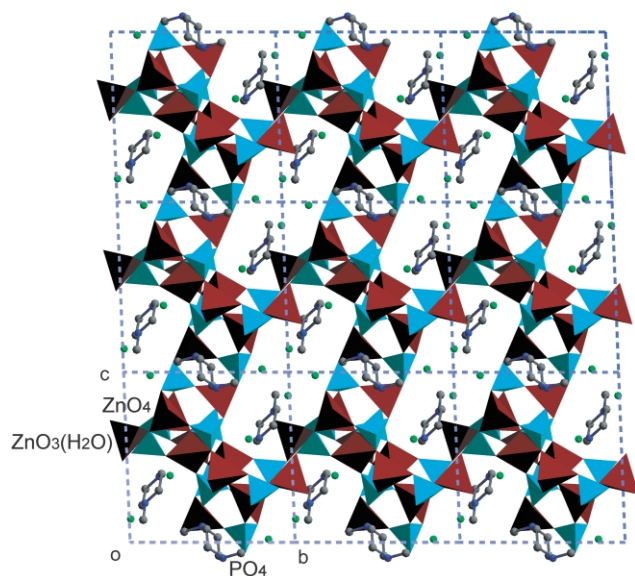
Fig. 2 Polyhedral view of the framework structure of phase **A** along the [100] direction showing the 16-membered ring channels.

The structure of **B** ($Zn_3(PO_4)_2H_2O$) exhibits a known framework without incorporation of the organic species.[16] Its structure consists of ZnO_4, $ZnO_4(H_2O)$ and PO_4 moieties linked through oxygen vertices forming an open-framework with 8-membered ring channels along the [010] direction.

The structure of **C** ($[Zn_5P_4O_{16}(H_2O)]\cdot C_4H_{14}N_2$)‡ is built up by ZnO_4, $ZnO_3(H_2O)$, PO_4 and $PO_3(=O)$ units *via* vertex oxygen atoms forming an open-framework with 10-membered ring channels along the [010] direction (Fig. 3). There also exist Zn–O–Zn bonds connected through μ_3-O atoms. Each 10-membered ring accommodates one diprotonated *N,N'*-dimethylethylenediamine molecule, which is believed to be decomposed from the *N,N'*-dimethylpiperazine molecules under hydrothermal conditions. The structure of **C** is similar to that of a reported hybrid zinc phosphate in which one end of diethylene-
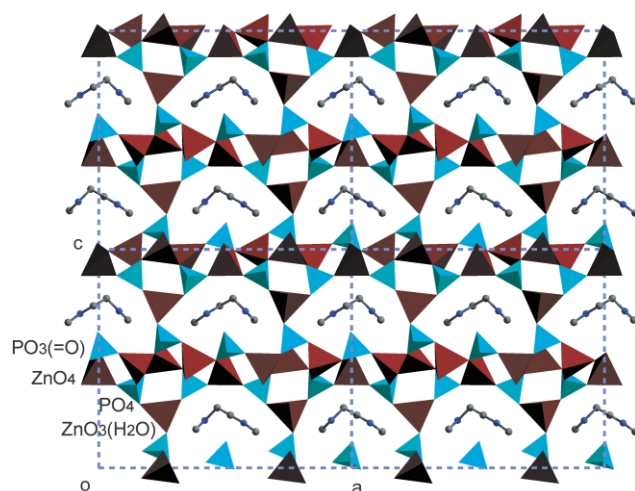
triamine templating molecule is coordinated to one Zn atom forming the Zn–N bond.[22]

Employing a combinatorial approach, new zinc phosphate compounds have been prepared under hydrothermal conditions. They exhibit interesting open-framework architectures and in particular, compound **A** has large 16-membered ring channels intersected with 10- and 8-membered ring channels. Their synthesis parameters are systematically investigated in a fast and efficient way. Hydrothermal combinatorial synthesis demonstrates its power for the discovery of new open-framework materials.

Notes and references

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Fig. 3 Polyhedral view of the framework structure of phase **C** along the [010] direction showing the 10-membered ring channels.