

# Assembly of one-dimensional $\text{AlP}_2\text{O}_8^{3-}$ chains into three-dimensional $\text{MAIP}_2\text{O}_8 \cdot \text{C}_2\text{N}_2\text{H}_9$ frameworks through transition metal cations ( $\text{M} = \text{Ni}^{2+}$ , $\text{Co}^{2+}$ and $\text{Fe}^{2+}$ )

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Three-dimensional (3D)  $\text{MAIP}_2\text{O}_8 \cdot \text{C}_2\text{N}_2\text{H}_9$  open-frameworks have been successfully generated from 1D  $\text{AlP}_2\text{O}_8^{3-}$  chains using transition metal cations  $\text{M}^{2+}$  ( $\text{M} = \text{Ni}$ ,  $\text{Co}$  and  $\text{Fe}$ ). The 1D  $\text{AlP}_2\text{O}_8^{3-}$  chain compound whose chain structure is made up of corner-sharing  $\text{Al}_2\text{P}_2$  four-membered rings is prepared solvothermally using ethylenediamine as a template; to the reactant mixture in which the one-dimensional  $\text{AlP}_2\text{O}_8^{3-}$  chain compound has already crystallized, transition metal cations are added. Structural analysis indicates that the terminal oxygen atoms attached to the one-dimensional  $\text{AlP}_2\text{O}_8^{3-}$  chains are exclusively coordinated to  $\text{M}^{2+}$  forming O–M–O bonds. XRD, DRS, ICP, CHN and Mössbauer techniques have been used to characterise the products. This work provides a new approach to the synthesis of 3D open-frameworks through the assembly of low-dimensional structures *via* transition metal cations.

## Introduction

Microporous materials are of considerable interest because of their widespread applications in the fields of catalysis, separation, adsorption and host–guest assembly.<sup>1–4</sup> However, because of the complexity of the synthetic chemistry and the poor understanding of the crystallization mechanism, the rational synthesis of these materials is full of difficulty.

The design and synthesis of microporous materials have received great attention.<sup>5–9</sup> So far, there are two main approaches towards the rational synthesis of microporous materials with specified structures and properties. One is based on the understanding of the relationship between the host (inorganic framework) and the guest (organic agents) with the aid of computers.<sup>10–18</sup> The other approach is based on a possible ‘built-up’ process from building units (BUs)<sup>19</sup> under suitable conditions. The building unit, which is a helpful tool for an easy description and analysis of the structures, has been successfully used to design and construct new classes of crystalline compounds that possess useful physical properties in the field of molecular sciences.<sup>20–25</sup> Open-framework structures can be assembled using metals or metal clusters as nodes and multifunctional organic ligands to link them. Yaghi *et al.*<sup>26</sup> reported the use of carboxylate-bridged metal clusters as metal–organic BUs to build extended self-assembled structures. Starting from one BU (the  $[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$  ion) known in solution, Sécheresse *et al.*<sup>27</sup> used the properties of alometric condensation of the polycation to generate in solution neutral or anionic wheels differing in their nuclearity, shape, and charge. The solids are then derived by tuning the type of associated cation that creates solids with dimensionalities ranging from 0 to 3. Recently, Rao *et al.* developed a ‘built-up’ principle for complex open-framework structures of metal phosphates with different dimensionalities.<sup>28</sup> A zero-dimensional zinc phosphate comprising 4-membered rings (MRs) has been isolated,<sup>29</sup> which is believed to be the starting BU involved in the formation of complex architectures. Many other complex inorganic structures are also likely to be designed from basic BUs and formed *via* self-assembly processes.

Our interests are focused on the organically templated aluminophosphates with rich structural and compositional diversities. Recently, we and others have successfully synthesized a variety of 1D,<sup>30–32</sup> 2D<sup>33–39</sup> and 3D aluminophos-

phates<sup>40–42</sup> with various Al/P ratios, such as 1 : 1, 1 : 2, 3 : 5, 2 : 3, 3 : 4, 4 : 5, 5 : 6, 11 : 12, 12 : 13 and 13 : 18. The structures of these materials are built up from an alternation of Al-centered polyhedra ( $\text{AlO}_4$ ,  $\text{AlO}_5$  and  $\text{AlO}_6$ ) and P-centered tetrahedra with one, two, three or four bridging oxygens. The lower dimensional structures including 1D chains and 2D layers exclusively contain terminal P–OH and/or P=O groups. The existence of terminal P–OH and P=O groups indicates that 3D open-frameworks can possibly be built up from lower dimensional chains or layers which may act as BUs through condensation reactions.<sup>7,31,36</sup>

The 1D  $\text{AlP}_2\text{O}_8^{3-}$  chain built up by corner-sharing  $\text{Al}_2\text{P}_2$  4-MRs is one of the most simple and fundamental structures among the aluminophosphates.<sup>32</sup> It is made up of alternating  $\text{AlO}_4$  and  $\text{PO}_2(\text{=O})_2$  tetrahedra. The existence of terminal P=O groups indicates that they might have potential in further condensation. Due to the restriction of Lowenstein’s rule, no P–O–P connections are allowed. The terminal P=O groups must be condensed across an extra Al or other metal species. The transition metal atom has a strong coordination affinity for oxygen and might have the potential to assemble the lower dimensional chains or networks into a 3D open-framework through coordination to terminal phosphoryl oxygen atoms. We have previously communicated the preparation of  $[\text{NiAlP}_2\text{O}_8][\text{C}_2\text{N}_2\text{H}_9]$  (NiAPO-1), a 3D open-framework through the assembly of 1D  $\text{AlP}_2\text{O}_8^{3-}$  chains *via*  $\text{Ni}^{2+}$  cations.<sup>43</sup> The structural solution of NiAPO-1 shows that an intact 1D chain structure is still present in NiAPO-1. The terminal oxygens of the 1D chains are exclusively coordinated to Ni atoms. Each Ni atom forms five Ni–O–P bonds and a Ni–N bond. An infinite –Ni–O–Ni– chain is formed through bridging  $\mu_3$ -O atoms. The 1D  $\text{AlP}_2\text{O}_8^{3-}$  chains and the –Ni–O–Ni– chains are cross-linked with each other forming a 3D framework with 8-MR windows. This suggests that 1D  $\text{AlP}_2\text{O}_8^{3-}$  chains acting as BUs can be assembled through  $\text{Ni}^{2+}$  cations to form the 3D framework. Herein, we further studied the assembly of the 1D chains *via* transition metal  $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$  cations, as well as  $\text{Ni}^{2+}$  cations. The assembly process of 1D chains and  $\text{Ni}^{2+}$  cations has been investigated in detail by XRD, ICP and DRS analyses. A possible assembly scheme is proposed. This work provides a new approach to the preparation of 3D frameworks through the assembly of low-dimensional structures with transition metal cations.

## Experimental

### Synthesis of the 1D $\text{AlP}_2\text{O}_8^{3-}$ chain compound

Firstly, the 1D aluminophosphate chain compound (compound **1**) was prepared in a gel with molar composition  $\text{Al}(i\text{-PrO})_3 : 5.0 \text{ H}_3\text{PO}_4 : 6.0 \text{ en} : 82.4$  ethylene glycol (EG). Typically, 0.4 g aluminium triisopropoxide was first dispersed into 9.0 mL of EG with stirring, followed by the addition of 0.79 mL of en, then 0.66 mL of  $\text{H}_3\text{PO}_4$  (85 wt% in water) was added dropwise. The reaction mixture was further stirred until it was homogeneous and then was loaded into a Teflon-lined stainless steel autoclave and heated at 180 °C for 5 days under static conditions.

### Assembly of the 1D $\text{AlP}_2\text{O}_8^{3-}$ chain via transition metal cations

$\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  were chosen as  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$  sources, respectively. After compound **1** had crystallized, certain amounts of transition metal cations was added to the reactant mixture (see Table 1). The mixture was further heated for about 10 days. The final product was filtered off, washed and dried at ambient temperature. The assembly products via  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$  cations are light-green, pink and light-green in color, respectively.

### Study on the assembly process

Several autoclaves with the same amount of reactant were put into an oven and heated under the same conditions. At one day intervals, an individual autoclave was taken out from the oven, followed by quenching in cold water immediately to stop the reaction. The solid and liquid samples were obtained by centrifugation.

### Characterization

X-Ray powder diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer with  $\text{Cu-K}\alpha$  ( $\lambda = 1.5418\text{\AA}$ ) radiation. The elemental analysis was carried out on a Perkin-Elmer 2400 Series II CHNS/O analyzer. Inductively coupled plasma (ICP) analysis was conducted on a Perkin-Elmer Optima 3300DV spectrometer. Diffuse reflection spectra (DRS) were taken on a Perkin-Elmer Lambda 20 UV-Vis diffuse reflection spectrometer at room temperature. The spectra were recorded against  $\text{BaSO}_4$  white reflectance standard in the range 200–850 nm. The Mössbauer measurements were carried out on an Oxford MS-500 Mössbauer instrument at room temperature. Isomer shift was reported with respect to an  $\alpha$ -iron foil standard.

## Results and discussion

### Synthesis and characterization of $\text{MAlP}_2\text{O}_8 \cdot \text{C}_2\text{N}_2\text{H}_9$ ( $\text{M} = \text{Ni}^{2+}$ , $\text{Co}^{2+}$ and $\text{Fe}^{2+}$ )

The 1D  $\text{AlP}_2\text{O}_8^{3-}$  chain compound (**1**) was first prepared using the  $\text{Al}(i\text{-PrO})_3\text{-H}_3\text{PO}_4\text{-en-glycol}$  system. To the reactant mixture in which compound **1** had already formed,  $\text{Ni}^{2+}$  species are introduced. Table 1 presents the influence of the amount of  $\text{Ni}^{2+}$  cations on the products. Without addition of  $\text{Ni}^{2+}$  species to the reactant, the product is still a 1D  $\text{AlP}_2\text{O}_8^{3-}$  chain compound even after crystallisation for 15 days. When the molar ratio of  $\text{Ni}(\text{OAc})_2/\text{Al}(i\text{-PrO})_3$  is in the range from 0.4 to 1.2, NiAPO-1 is produced accompanied by compound **1**. With an increase in the  $\text{Ni}(\text{OAc})_2/\text{Al}(i\text{-PrO})_3$  molar ratio, the proportion of NiAPO-1 increases in the final product. When the molar ratio of  $\text{Ni}(\text{OAc})_2/\text{Al}(i\text{-PrO})_3$  is over 1.6, pure light-green crystals of NiAPO-1 are obtained.

These results show that  $\text{Ni}^{2+}$  plays an important role in the assembly of 1D  $\text{AlP}_2\text{O}_8^{3-}$  chains into a 3D open-framework.

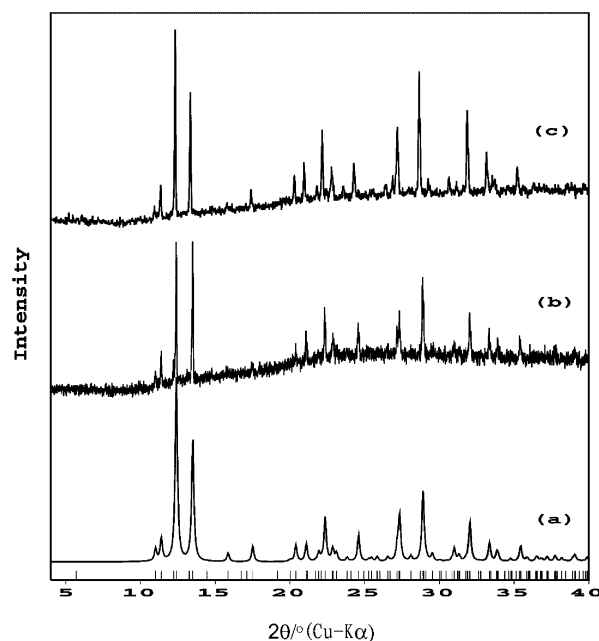
**Table 1** Influence of the molar ratio of  $\text{M}^{2+}/\text{Al}(i\text{-PrO})_3$  on the product

$\text{M}^{2+}$ source	$\text{M}^{2+}/\text{Al}(i\text{-PrO})_3$	Product
$\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$	0	<b>1</b>
	0.4	<b>1</b> and NiAPO-1
	0.8	<b>1</b> and NiAPO-1
	1.2	NiAPO-1 and <b>1</b>
	1.6–5.0	NiAPO-1
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	0	<b>1</b>
	0.5–1.0	<b>1</b> and CoAPO-1
	1.5	CoAPO-1 and <b>1</b>
	2.0–2.5	CoAPO-1
	3.0	CoAPO-1 + $\text{CoPO}_4$
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	0	<b>1</b>
	0.7	<b>1</b> and FeAPO-1
	1.0	FeAPO-1 and <b>1</b>
	1.3–2.0	FeAPO-1

Temperature: 180 °C. Crystallization time: 10 days.

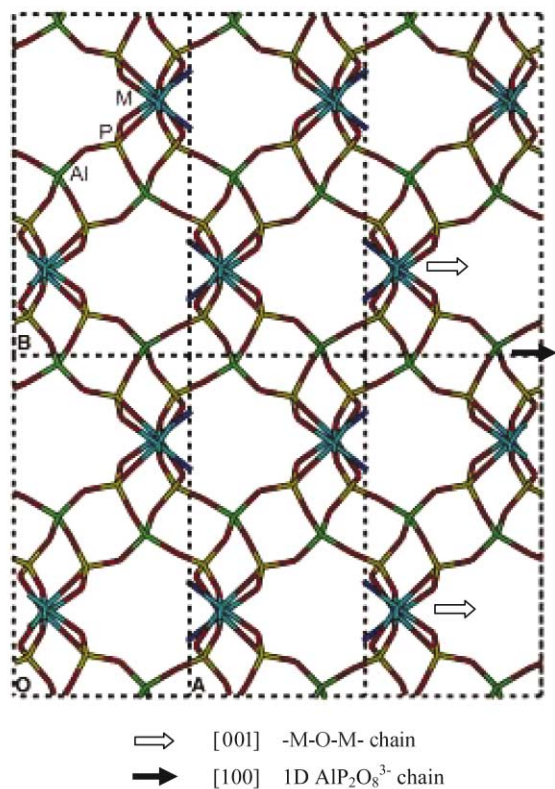
Since Fe and Co atoms are congeners of the Ni atom, they could also possibly be employed in the assembly of 1D  $\text{AlP}_2\text{O}_8^{3-}$  chains into 3D framework. By using a similar approach,  $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$  cations are introduced into the mixture in which compound **1** is crystallized. The experimental conditions and results are listed in Table 1. The assembly products of the 1D chains with  $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$  are denoted as CoAPO-1 and FeAPO-1, respectively. The appropriate molar ratios of  $\text{M}^{2+}/\text{Al}(i\text{-PrO})_3$  ( $\text{M} = \text{Co}^{2+}$  and  $\text{Fe}^{2+}$ ) for CoAPO-1 and FeAPO-1 are 2.0–2.5 and 1.3–2.0, respectively.

A cobalt-containing aluminophosphate  $\text{CoAlP}_2\text{O}_8 \cdot \text{C}_2\text{N}_2\text{H}_9$ <sup>44</sup> with a structure analogous to NiAPO-1 has been reported before; this was prepared hydrothermally in the  $\text{CoO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-en-H}_2\text{O}$  system. The XRD patterns of CoAPO-1 and FeAPO-1 are shown in Fig. 1(b) and (c), respectively, which are



**Fig. 1** (a) Simulated XRD pattern of  $\text{CoAlP}_2\text{O}_8 \cdot \text{C}_2\text{N}_2\text{H}_9$ , and experimental XRD patterns of (b) CoAPO-1 and (c) FeAPO-1.

consistent with that simulated from the single crystal structure data of  $\text{CoAlP}_2\text{O}_8 \cdot \text{C}_2\text{N}_2\text{H}_9$ .<sup>44</sup> XRD studies indicate that the structures of CoAPO-1 and FeAPO-1 are analogous to those of  $\text{CoAlP}_2\text{O}_8 \cdot \text{C}_2\text{N}_2\text{H}_9$  and NiAPO-1. Fig. 2 shows the structural model of MAPO-1 ( $\text{M} = \text{Co}^{2+}$  and  $\text{Fe}^{2+}$ ) based on the structure of NiAPO-1. The 1D  $\text{AlP}_2\text{O}_8^{3-}$  chains are assembled into 3D open-frameworks by  $\text{M}^{2+}$  cations in such a way that all the

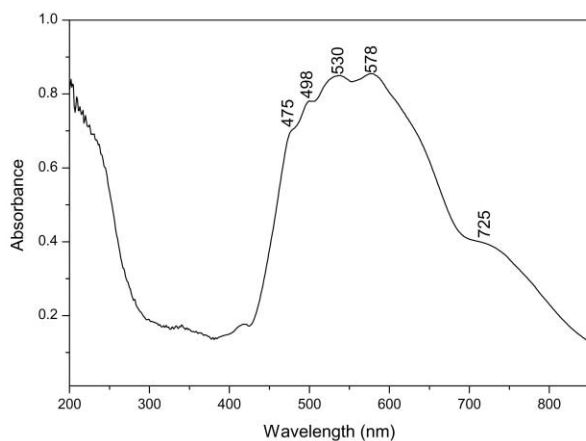


**Fig. 2** The structural model of CoAPO-1 and FeAPO-1 based on the crystal structure of NiAPO-1.

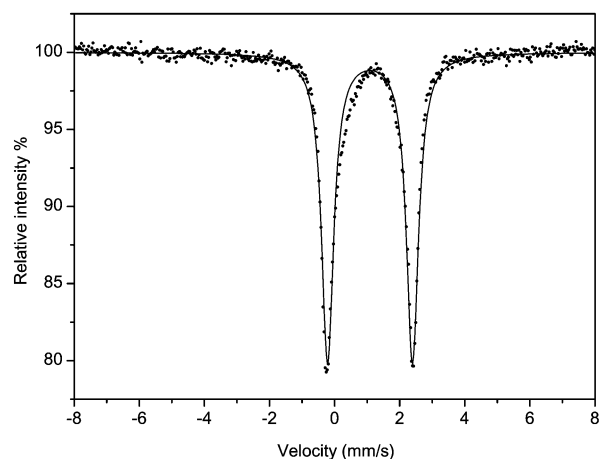
terminal oxygen atoms attached to the 1D  $\text{AlP}_2\text{O}_8^{3-}$  chains are exclusively coordinated to  $\text{M}^{2+}$  forming O–M–O bonds. Each  $\text{M}^{2+}$  cation is coordinated to five terminal oxygens and one N atom of en to form an octahedron.

Chemical analysis of the product gives the atomic ratio of Co/Al/P/C/N/H to be 1.00 : 1.06 : 2.15 : 1.98 : 1.92 : 9.00, which is in good agreement with the empirical formula of  $\text{CoAlP}_2\text{O}_8 \cdot \text{C}_2\text{N}_2\text{H}_9$ . Chemical analysis of FeAPO-1 gives the molar ratio of Fe/Al/P/C/N/H to be 1.00 : 0.92 : 1.74 : 2.09 : 2.02 : 9.01, suggesting that it has a similar empirical formula of  $\text{FeAlP}_2\text{O}_8 \cdot \text{C}_2\text{N}_2\text{H}_9$ .

The DRS spectrum of CoAPO-1 is presented in Fig. 3, with absorptions at 475, 498, 530, 578 and 725 nm, respectively. The former four absorptions have been observed in  $\text{Co}(\text{HPO}_4)_2(\text{OH})_2$  for  $\text{Co}^{2+}$  in an octahedral environment.<sup>45</sup> The low-frequency band at 725 nm is characteristic of  $\text{Co}^{2+}$  in a distorted octahedral symmetry. This assignment is consistent with the unusual  $\text{Co}^{2+}$  coordination in  $\text{CoAlP}_2\text{O}_8 \cdot \text{C}_2\text{N}_2\text{H}_9$ , determined by the single-crystal X-ray diffraction analysis.<sup>44</sup>



**Fig. 3** Diffuse reflectance spectrum of as-synthesized CoAPO-1.



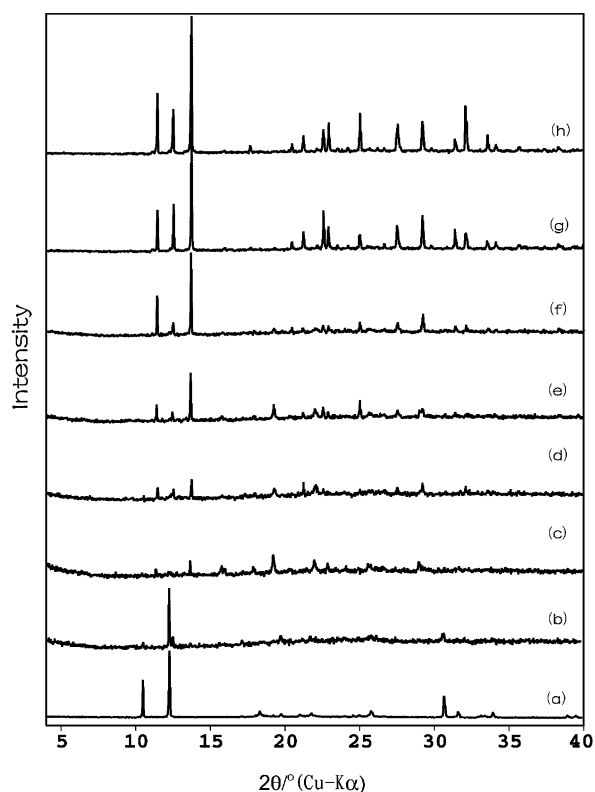
**Fig. 4** Mössbauer spectrum of FeAPO-1 at room temperature.

Mössbauer spectroscopy carried out at room temperature indicates that the valence state of Fe in FeAPO-1 is +2 (Fig. 4). A quadrupole doublet characteristic of high-spin +2 iron is observed.<sup>46,47</sup> The obtained isomer shift ( $\delta$ ) (relative to natural iron foil) and quadrupole splitting ( $\Delta E$ ) are  $\delta = 1.19 \text{ mm s}^{-1}$  and  $\Delta E = 2.61 \text{ mm s}^{-1}$ , respectively, which are similar to that of octahedrally coordinated  $\text{Fe}^{2+}$  in  $\text{NH}_4\text{Fe}_2(\text{PO}_4)_2$ .<sup>48</sup> This result suggests that  $\text{Fe}^{2+}$  in FeAPO-1 is in octahedral symmetry, the same as that of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  in CoAPO-1 and NiAPO-1, respectively.

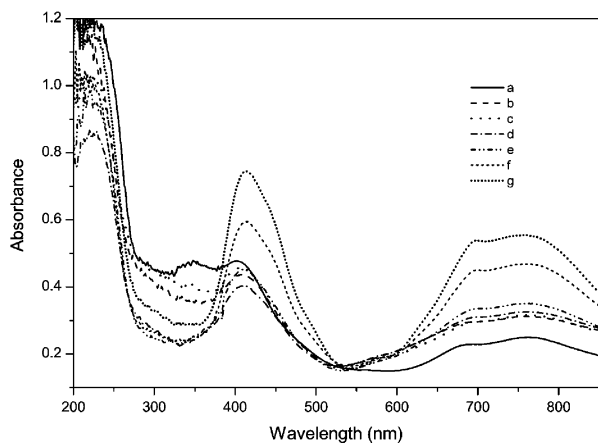
#### Studies on the assembly process

The above results indicate that  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$  cations can be used to assemble 1D  $\text{AlP}_2\text{O}_8^{3-}$  chains into 3D open-frameworks. In order to obtain some formation information, the assembly process of 1D  $\text{AlP}_2\text{O}_8^{3-}$  chains *via*  $\text{Ni}^{2+}$  cations has been further studied by XRD, DRS and ICP analyses. XRD study on the samples collected from the reaction mixture at various time intervals during the assembly process is shown in Fig. 5. Fig. 5(a) shows the XRD pattern of the 1D aluminophosphate chain compound **1** after crystallisation for 5 days before the addition of the  $\text{Ni}^{2+}$  species. After the addition of  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  followed by further heating at  $180^\circ\text{C}$  for 1 day, the solid product contains mainly compound **1**. It is noted that with the increase of crystallization time, NiAPO-1 gradually dominates in the product with the decrease of compound **1**, which suggests that some of the 1D chains have been transformed into a 3D open-framework. After heating for about 10 days, a pure phase of NiAPO-1 is obtained.

DRS spectra are applied to study the change of  $\text{Ni}^{2+}$  in the solid samples (Fig. 6). The framework of NiAPO-1 contains only six-coordinated  $\text{Ni}^{2+}$  atoms. For octahedral  $\text{Ni}^{2+}$ , three spin-allowed electronic transitions are expected, and two of them are within the visible region.<sup>49–51</sup> The expected absorption bands for octahedral nickel in the visible region are clearly observed at about 410 and 695–765 nm in this sample. Careful inspection of the spectrum reveals the presence of the two peaks at 696 and 765 nm, respectively. The 410 nm band is due to one of the spin-allowed electronic transitions in the visible region ( ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{D})$ ). The band at 765 nm is assigned to the other spin-allowed electronic transition in the visible region ( ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ ). The bands at about 410 and 765 nm are typical DRS absorption bands for  $\text{Ni}^{2+}$  in an octahedral symmetry. The 695 nm band is ascribed to the presence of a spin-forbidden transition that may be introduced by the spin-orbit coupling in “mixing” a spin singlet ( ${}^1\text{E}_g$ ) with the  ${}^3\text{T}_{1g}(\text{F})$  spin triplet. However, the bands at 695 and 765 nm are not in conformity with those in regular octahedral symmetry.<sup>49</sup> This is in good agreement with the result of the single crystal



**Fig. 5** XRD study on the assembly process: (a) as-synthesized compound **1** and the samples after further crystallization for (b) 1 d, (c) 2 d, (d) 3 d, (e) 5 d, (f) 7 d, (g) 9 d, and (h) 10 d with the addition of  $\text{Ni}^{2+}$  cations.

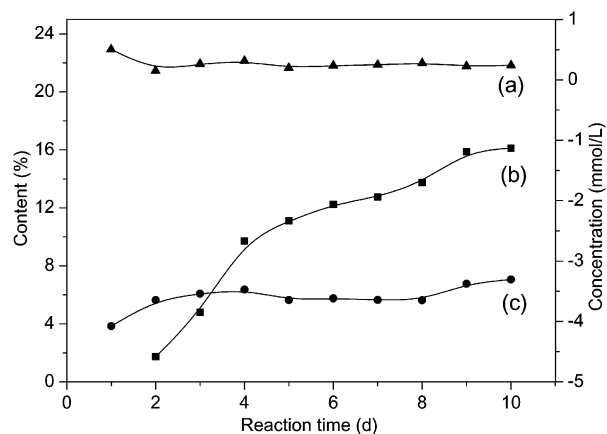


**Fig. 6** Diffuse reflectance spectra of samples collected during the assembly process with the addition of  $\text{Ni}^{2+}$  cations: (a) 1 d, (b) 2 d, (c) 3 d, (d) 5 d, (e) 7 d, (f) 9 d, and (g) 10 d.

X-ray diffraction analysis, which shows that the Ni atom is in a distorted octahedral symmetry.

Weckhuysen *et al.*<sup>52</sup> found that the intensity of the d–d transition of  $\text{Co}^{2+}$  and  $\text{V}^{4+}$  more or less linearly increases with the increase of metal loading in the aluminophosphate framework, and suggested that DRS spectra could be used to quantify the amount of the transition metal cation in the as-synthesized materials by integrating the intensity in the frequency region of certain absorption bands. The increase of the intensity of the d–d transition with reaction time implies that more and more  $\text{Ni}^{2+}$  cations participate in the assembly of 1D  $\text{AlP}_2\text{O}_8^{3-}$  chains into the 3D open-framework (Fig. 6). This is in accordance with the increase of the crystallinity of NiAPO-1 during the assembly process determined by powder XRD analysis.

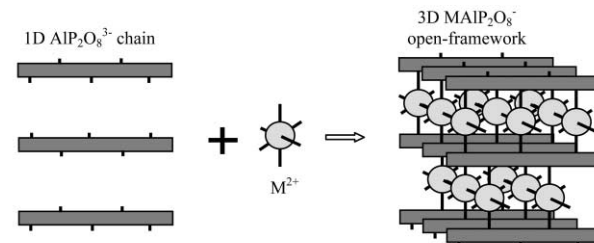
Compositional analysis of the solid and liquid samples will give further helpful information on the assembly process. The variation of the concentration of Al in the liquid phase is plot-



**Fig. 7** (a) The variation of Al concentration in solution and the changes of (b) Ni and (c) Al content in the solid sample with reaction time.

ted as a function of the reaction time (Fig. 7a). It is noted that the concentration of Al in the solution is rather low ( $0.15\text{--}0.50\text{ mmol L}^{-1}$ ) and its variation is very small. The changes of the content of Al and Ni in the solid phase are shown in Fig. 7. Consistent with that in solution, the content of Al in the solid phase shows little variation during the assembly with  $\text{Ni}^{2+}$  cations. It is noteworthy that the content of Ni in the solid phase increases gradually with reaction time (Fig. 7b), which implies that more and more  $\text{Ni}^{2+}$  species from the solution react with the 1D  $\text{AlP}_2\text{O}_8^{3-}$  chains to generate the NiAPO-1 open-framework.

Our studies have shown that the 1D  $\text{AlP}_2\text{O}_8^{3-}$  chains can be assembled into 3D open-frameworks through transition metal cations  $\text{M}^{2+}$  ( $\text{M} = \text{Ni}, \text{Co}$  and  $\text{Fe}$ ). A possible scheme for the assembly process from 1D  $\text{AlP}_2\text{O}_8^{3-}$  chains into a 3D open-framework is proposed in Fig. 8. The  $\text{M}^{2+}$  species added to the



**Fig. 8** A possible scheme for the assembly pathway in the formation of the 3D open-framework from the 1D  $\text{AlP}_2\text{O}_8^{3-}$  chains through transition metal cations.

reactant mixture in which compound **1** has been crystallized interact with the terminal phosphonyl groups of the 1D  $\text{AlP}_2\text{O}_8^{3-}$  chains and the en molecules located in the interchain region to form 3D open-frameworks. The present work provides a new approach to the preparation of 3D open-framework structures by the assembly of low-dimensional structure acting as BUs *via* transition metal cations.

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