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Synthesis of Cobalt-Zinc Phosphates Templated by Polyamines

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1. Introduction

Open-framework structures of metal phosphates, especially those zinc and cobalt phosphates, have exhibited many fascinating structural features and potential applications in catalysis, separation processes, and as photoluminantphosphors (Rao et al., 2000; Chang et al., 2004). The feasibility of zinc and cobalt to tetrahedrally coordinate their phosphates makes them to be an important group of transition metal phosphates (Mandal & Natarajan, 2002; Harrison et al., 1991; Neeraj et al., 1999; Fan et al., 2000). Usually, these materials have been synthesized by employing hydrothermal or solvothermal conditions in the presence of organic amines as the structure-directing agents (SDA). Studies have shown that the important role of host–guest charge matching between the inorganic frameworks and the organic amines makes linear polyamines the preferred candidates for the structure-directing agents to form the higher negative charge framework of zinc and cobalt phosphates (Bu et al., 1997, 1998; Feng et al., 1997). Moreover, diethylenetriamine (DETA), triethylenetetramine (TETA) and tetraethylenepentamine (TEPA) become typical amines and have directed the formation of a large number of open-framework structures of zinc (or cobalt) phosphates by varying their concentrations accompanying with the changes in inorganic compositions (Choudhury et al., 2000).

Recently, a new synthesis route involving alkylformamide as a template precursors has been reported (Lakiss et al., 2005; Vidal et al., 2000). It seems that organic amines generated in situ by the decomposition of alkylformamide show a special effect on the formation of metal phosphates with a novel structure. In our studies aimed to synthesize transition metal phosphates, more than one cobalt-zinc phosphates with different framework structures have been obtained from a single gel using diethylenetriamine as the organic basis (Lu et al., 2008; Li et al., 2009). It is noticed that the guest species encapsulated in their structures are not diethylenetriamine, but some smaller amines decomposed from it. Controlling the in situ decomposition of these linear polyamines plays the key role for directing the synthesis of pure-phase cobalt-zinc phosphates. According to these matters, large amines can also be used as a source for smaller amines as they will provide hydrolysis decomposition in the reaction mixture during crystallization. In the synthesis a temperature of crystallization is an important factor for controlling the hydrolysis of linear polyamines, and higher temperature makes decomposition of polyamines easier. On the other hand, adding small amines, such as propylamine, butylamine, can control the decomposition of the chain-type polyamines.

2. Three open-framework cobalt-zinc phosphates synthesized in the presence of linear polyamines as structure-directing agents (SDA)

In this section, three unique frameworks of cobalt-zinc phosphate have been synthesized under hydrothermal or solvothermal conditions. They were named as $CoZnPO_4$-IV, $CoZnPO_4$-V and $CoZnPO_4$-VI, respectively. $CoZnPO_4$-IV with cross-linked 10- and 8-ring channels was synthesized in the presence of diethylenetriamine. $CoZnPO_4$-V with cross-linked 16-, 12- and 10-ring channels was synthesized using diethylenetriamine as a structure-directing agent. $CoZnPO_4$-VI has 16-ring one-dimensional channels. It was synthesized in the presence of triethylenetetramine. Polyamines did not decompose during the synthesis process (Fig.13d, 13e, and 13f). Extra-large-pore structures ($CoZnPO_4$-V and $CoZnPO_4$-VI) with 16-ring channels have been synthesized in the presence of linear polyamines as the structure-directing agents (SDA).

2.1 Synthesis and initial characterization

The main reactants are $Zn(CH_3COO)_2$ (denoted as $ZnAc_2$), $Co(CH_3COO)_2$ (denoted as $CoAc_2$), H_3PO_4, linear polyamines, and ethylene glycol. In a typical synthetic procedure, solution A was prepared by mixing $ZnAc_2 \cdot 2H_2O$ with 85% H_3PO_4 and ethylene glycol (EG), the mixture was stirred at room temperature until $ZnAc_2 \cdot 2H_2O$ was dissolved. Solution B was prepared by mixing $CoAc_2 \cdot 4H_2O$, distilled water, and 85% H_3PO_4. Solution A and a kind of linear polyamine, such as diethylenetriamine were added to solution B. Then the pH value of the mixture was adjusted to 8.0 by adding an assistant amine. Finally the mixture was transferred to a stainless steel autoclave and heated at 140˚C~160˚C for 3-10 days. Specific gel compositions and crystallization conditions of three cobalt-zinc phosphates are shown in Table.1. (In the synthesis of $CoZnPO_4$-VI, drips of HF(40%) were added to the gel).

Sample	Reactant composition						Crystallization condition	
	ZnO	CoO	H_3PO_4	polyamine	H_2O	EG	Temp/ ^oC	Time/day
$CoZnPO_4$-IV	2.0	1.0	10.5	1.8DETA	300	0	160	3
$CoZnPO_4$-V	2.0	1.0	9.0	1.8DETA	95.4	9.6	140	10
$CoZnPO_4$-VI	2.4	0.6	4.0	2.0TETA	400	0	140	4.5

Table 1. Gel compositions and crystallization conditions of three cobalt-zinc phosphates.

Three large vivid blue crystal ($CoZnPO_4$-IV, $CoZnPO_4$-V and $CoZnPO_4$-VI) have been synthesized hydrothermally. Scanning electron micrograph (SEM) images show their morphologies being distinct from each other as rectangular-like, rectangular column, thin plate-like, respectively (Fig.1). XRD patterns of the three compounds also show their phases being distinct from each other (Fig.1).

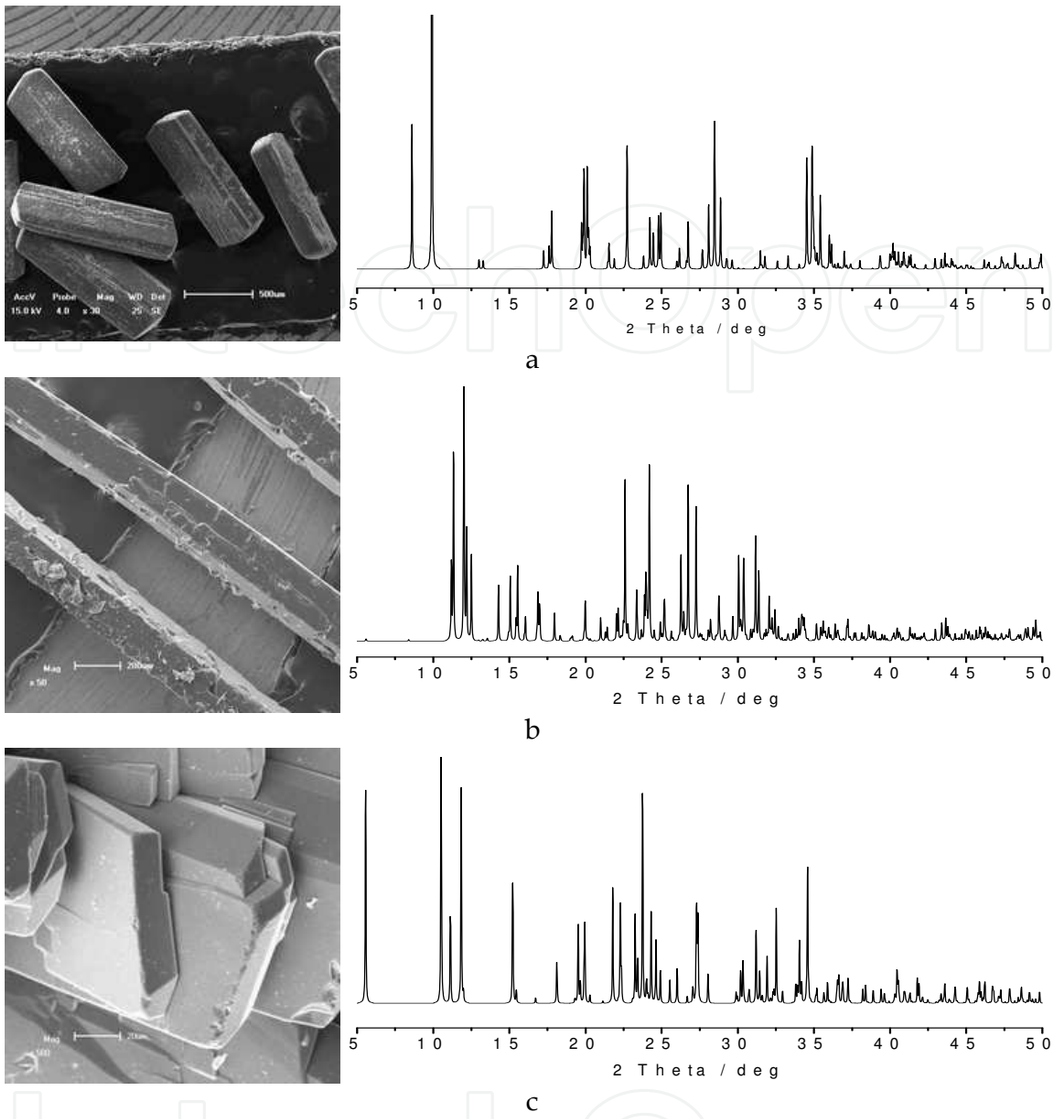


Fig. 1. Scanning electron micrograph (SEM) images and XRD patterns of the three compounds(a) $CoZnPO_4$-IV; (b) $CoZnPO_4$-V; (c) $CoZnPO_4$-VI.

2.2 Crystal structure of $CoZnPO_4$-IV

Single crystal analysis and Inductively Coupled Plasma atomic emission spectroscopy (ICP) analysis reveal that $CoZnPO_4$-IV is composed of $C_4N_3H_{15}Zn_{4.12}Co_{0.88}$ P_4O_{16}; it crystallizes in the monoclinic system, space group *Cc* (No. 9), with a = 26.926(7) Å, b = 5.1912(10) Å, c = 17.834(6) Å, α = γ = 90°, β = 130.25(2)°, V = 1902.6(9) Å^3, and z = 4.

The secondary structural unit of $CoZnPO_4$-IV is shown in Fig.2a, and it is composed of 3-rings and 4-rings. Secondary structural units link with each other through sharing oxygen atoms to form the layers along *ac*-plane. Then neighboring layers link with each other along *b*-axis, resulting in cross-linked 10- and 8-ring channels in $CoZnPO_4$-IV (Fig.2b). The 8-ring channels locate among the layers (Fig.2c).

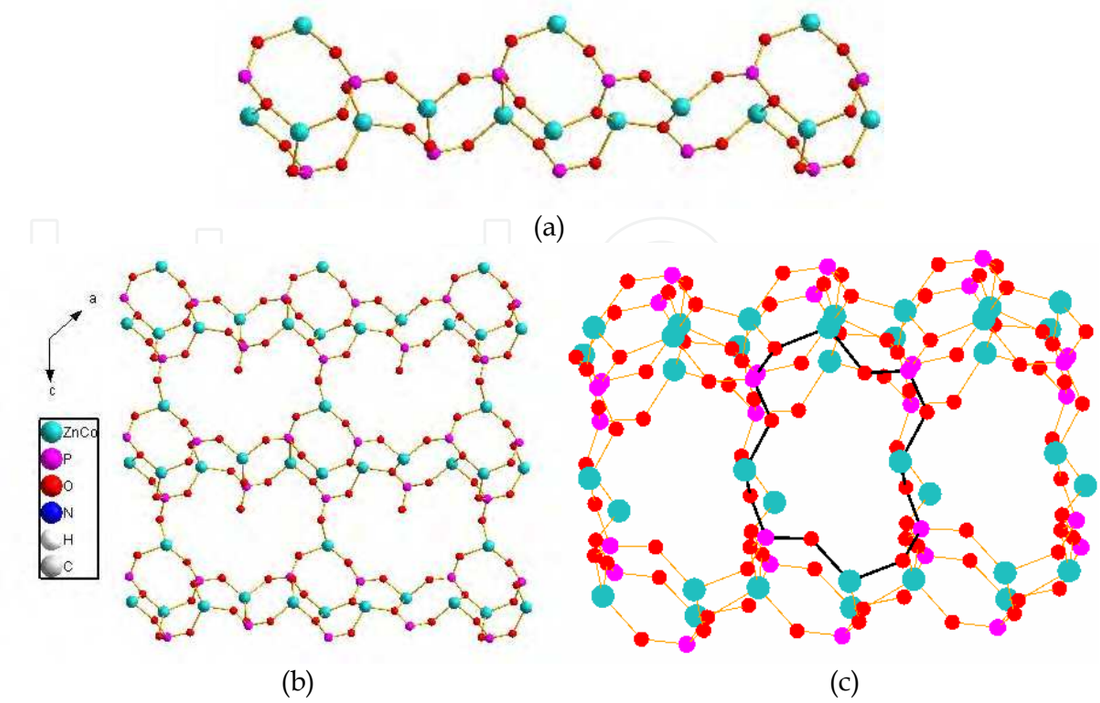


Fig. 2. (a) The secondary structural unit of $CoZnPO_4$-IV; (b) Structure of 10-rings along *ac*-plane in $CoZnPO_4$- IV; (c) Structure of 8-ring channel in $CoZnPO_4$- IV.

2.3 Crystal structure of $CoZnPO_4$-V

Single crystal analysis and Inductively Coupled Plasma atomic emission spectroscopy (ICP) analysis reveal that $CoZnPO_4$-V is composed of $C_{12}N_9H_{52}Zn_{4.5}Co_{1.5}P_8O_{32}$; it crystallizes in the monoclinic system, space group $P2_1/c$ (No. 14), with a = 31.936(3) Å, b = 8.3775(7) Å, c = 15.7874(13) Å, α = γ = 90°, β = 97.0530(10)°, V = 4191.8(6) Å^3, and z = 4.

Three edge-shared 4-ring units of Zn-O and P-O tetrahedral groups could be the building unit, which was named as 4^3 unit (Fig. 3a). The neighboring units link with each other through 4-ring to form an infinite zigzag chain along the *b*-axis direction (Fig. 3b). 2D (4, 10) nets are conformably formed of the chains of 4-ring units from the corner-shared 4^3 units (Fig. 3b).

Viewed along the plane parallel to *b*-axis, the neighboring 4^3 units link with each other in a corner- shared way to form another infinite chain (Fig. 3c). The neighboring chains link together from 4-ring every two 4^3 units to form a layer. Therefore, 16-ring channels are constructed (Fig. 3c). On the other hand, the wall of each 16-ring channel can be described as the coiling of a net composed of 10-rings and infinite 4-ring zigzag chain (Fig. 3b).

2.4 Crystal structure of $CoZnPO_4$-VI

Single crystal analysis and Inductively Coupled Plasma atomic emission spectroscopy (ICP) analysis reveal that $CoZnPO_4$-VI is composed of $C_6N_4H_{22}Co_{0.16}Zn_{5.84}(PO_4)_4(HPO_4)_2$; it crystallizes in the triclinic system, space group $P\bar{1}$ (No. 2), with a = 5.1919(10) Å, b = 8.7263(17) Å, c = 16.000(3) Å, α =89.07(3)°, β = 83.45(3)°, γ = 74.34(3)°, V = 693.4(2) Å^3, and z = 1.

The three-dimensional framework of $CoZnPO_4$-VI can be described by with two secondary structural units (SBU-a and SBU-b). SBU-a (Fig.4a) is a special structure composed of two 6-rings ladder linked face to face; SBU-b (Fig.4b) is a common 4-ring ladder in the molecular sieves. The linkage of SBU-a conducted by sharing 4-rings form the layers along *ab*-plane. SBU-a and SBU-b connect with one sharing oxygen atom in the structure, forming the three-dimensional framework of $CoZnPO_4$-VI and resulting in 16-ring large channels along the direction of *c*-axis (Fig.4c). The arms of channels are constituted mainly by SBU-a and SBU-b.

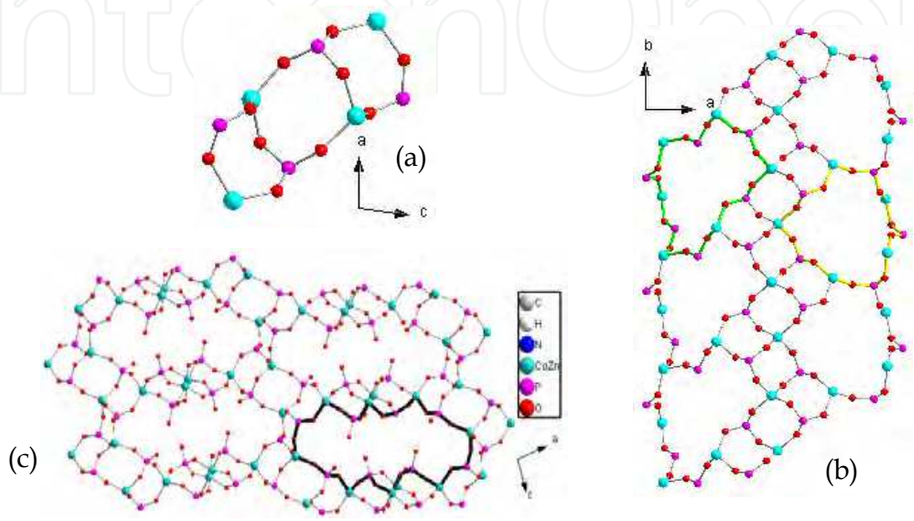


Fig. 3. (a) 4^3 unit along b-axis in $CoZnPO_4$-V; (b) Structure of 10-rings along *ab*-plane in $CoZnPO_4$-V. (c) Structure of 16-rings along *ac*-plane in $CoZnPO_4$-V.

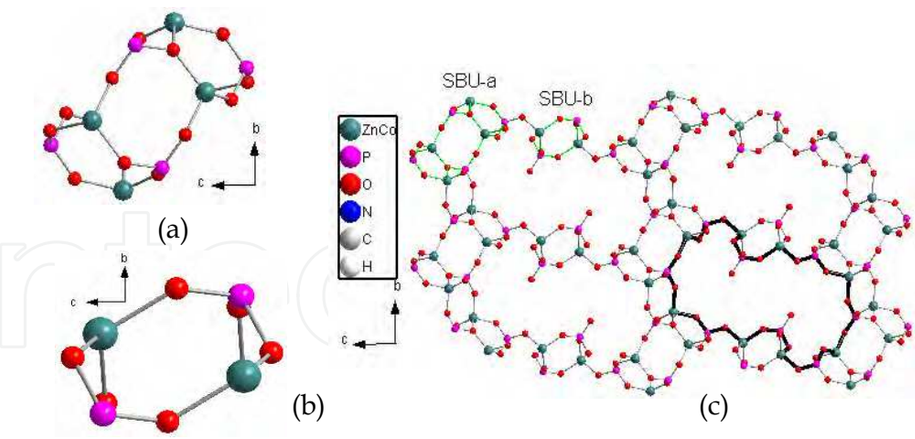


Fig. 4. (a) SUB-a; (b) SUB-b; (c) Structure of 16-rings along *bc*-plane in $CoZnPO_4$-VI.

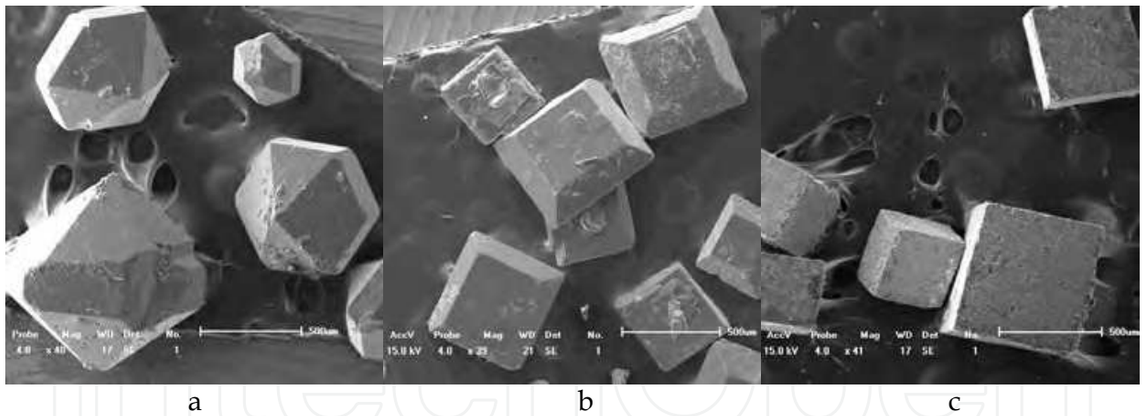
3. Controlling the in situ decomposition of linear polyamines to synthesize open-framework cobalt-zinc phosphates

As the organic templates, linear polyamines are easy to decompose at high reaction temperature (higher than 160°C) in the hydrothermal condition to synthesize microporous metal phosphate materials. In this section, three open-framework cobalt-zinc phosphates,

$CoZnPO_4$-I, $CoZnPO_4$-II, and $CoZnPO_4$-III, have been synthesized from a single gel at 200 °C. Organic amine in the starting mixture is diethylenetriamine. Structural analysis reveals that species encapsulated in the structures of $CoZnPO_4$-I, $CoZnPO_4$-II, and $CoZnPO_4$-III are ammonium, ethylenediaminum, and diethylenetriaminum, respectively, which can be attributed to the partly in situ decomposition of diethylenetriamine molecules during the crystallization procedure (Fig.13a, 13b, and 13c). When a second small organic amine, such as propylamine, or butylamine, was added to reacting mixture, single phase of $CoZnPO_4$-I, $CoZnPO_4$-II, or $CoZnPO_4$-III can be obtained respectively, according to the kind or concentration of small organic amine, which plays an important role on controlling the in situ decomposition of linear polyamines.

3.1 Synthesis and initial characterization

The main reactants are $ZnAc_2$, $CoAc_2$, H_3PO_4, DETA, and ethylene glycol. In a typical synthesis procedure, solution A was prepared by mixing $ZnAc_2$ $2H_2O$ (2.217 g) with 85% H_3PO_4 (0.98 mL) and ethylene glycol (EG) (2.7 mL), and then stirring at room temperature until $ZnAc_2$ $2H_2O$ was dissolved. Solution B was prepared by mixing $CoAc_2$ $4H_2O$ (1.252 g), distilled water (8.6 mL), and 85% H_3PO_4 (2.6 mL). Solution A and DETA (0.97 mL) were added to solution B. The pH value of the mixture was adjusted to pH 8.0 by the addition of *n*-propylamine (4.5 mL). The final molar ratio of the mixture was $2ZnAc_2 \cdot 2H_2O$:$1CoAc_2 \cdot 4H_2O$:9.6EG:10.5H_3PO_4:95.4H_2O:1.8DETA. The mixture was then transferred to a stainless steel autoclave and heated at 200 °C for 6 days. Three types of large blue crystal were filtered and washed with deionized water and dried in air.



a b c

Fig. 5. SEM images of the large crystals of three cobalt-zinc phosphates : (a) crystal of $CoZnPO_4$-I with elongated hexagonal-dipyramid morphology;(b) $CoZnPO_4$-II crystal with square bifrustum morphology; (c) $CoZnPO_4$-III crystal with cubical-like morphology.

Three open-framework cobalt-zinc phosphates have been synthesized hydrothermally from a single gel at 200°C by using DETA as the SDA with *n*-propylamine as the assistant organic amine. They are all large vivid blue crystals with sizes more than 400 μm. Scanning electron micrograph (SEM) images show their morphologies being distinct from each other, shaped as elongated hexagonal-dipyramid, square bifrustum, and cubical, respectively (Fig.5). XRD patterns of $CoZnPO_4$-I, -II, and -III (Fig.6) have shown that they are three distinguishing phases with different diffraction peaks.

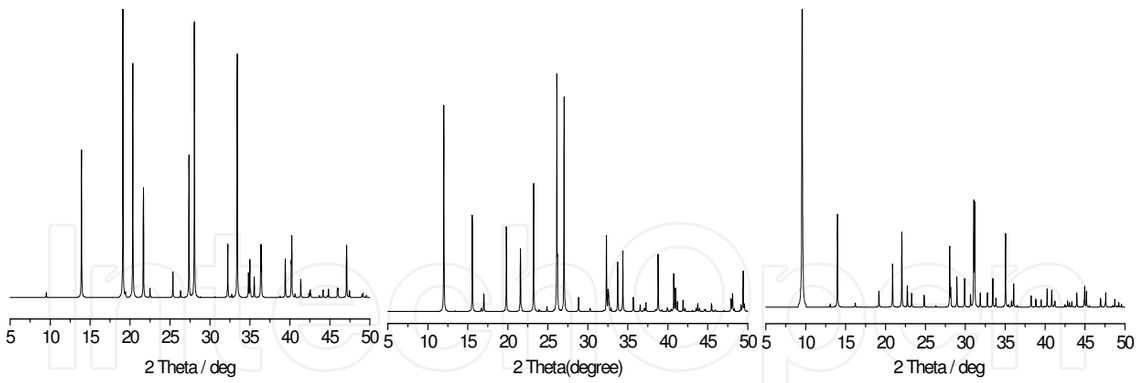


Fig. 6. XRD patterns of three cobalt-zinc phosphates: (a) $CoZnPO_4$-I; (b) $CoZnPO_4$-II; (c) $CoZnPO_4$-III.

3.2 Crystal structures of three compounds

It is clear that there are only diethylenetriamine and *n*-propylamine as the SDAs present in the starting materials. However, organic species encapsulated in the structure of $CoZnPO_4$-I, -II, and -III are ammonium, ethylenediaminum, and diethylenetriaminum cations, respectively (Fig.13a, 13b, 13c). The appearance of ethylenediaminum and ammonium may be attributed to the in situ decomposition of diethylenetriamine during the crystallization.

Single crystal analysis reveals that $CoZnPO_4$-I is a novel cobalt-zinc phosphate. It is composed of $(NH_4)_2Co_{0.34}Zn_{1.66}(PO_4)_2$, which was modeled as $(NH_4)_2Co_2(PO_4)_2$ in the single crystal data and crystallizes in the hexagonal system, space group $P6_3$ (No. 173), with $a = b = 10.7207(5)$Å, $c = 8.7241(8)$ Å, $\alpha = \beta = 90°$, $\lambda = 120°$, V=868.36(10) Å^3, and $z = 4$. Viewing along the plane parallel to *c*-axis, a net consisting of 6-ring channels has been found. The 6-ring channels with regularly alternating Zn(Co)- and P-centered tetrahedral can be considered as the building units of $CoZnPO_4$-I (Fig. 7a). J. V. Smith determined a simple hexagonal net, which has only one type of 3-connected node and is described as the Schläfli symbol 6^3 because each node lies between three circuits of 6 nodes (Smith, J. V. *Am. Mineral.* 1977).For any node in a simple hexagonal net in horizational position, an additional perpendicular linkage pointing either upward (U) or downward (D) may result in the linkage joined to a node of another simple hexagonal net lying either above or below the first hexagonal net. Eight ways of the sequence of U and D linkages around each 6-ring has been used to enumerate 4-connected, 3-dimensional nets and classification of framework of silicates and aluminophosphates.

The linking sequences of UDUDUD around each 6-ring produces a dense tridymite framework, whereas the UUUDDD results in an open framework ABW containing 8-ring channels. However, infinity of frameworks can be produced if more than one sequence occurs in the hexagons of a 6^3 net. This has just happened in the structure of $CoZnPO_4$-I. In its framework, the 6-rings of tetrahedral are present in two different conformations based on the more than one type circuit as the following sequence of up and down tetrahedral: UDUDUD and UUUDDD in the proportion 1:3. A second building unit, which is called a $6^9 4^6$cage, has been formed (Fig. 13a).

On the other hand, it can be found along the (010) plane that double 4-rings and one 6-ring linked in turn by sharing edges to form an infinite chain (Fig. 7b). These chains are cross-linked along the *c*-axis direction to the similar chains from the linkage Zn-O-P or P-O-Zn to form the sheet structure with edgesharing infinite 10-ring chains (Fig. 7b). Adjacent sheets are cross-linked with each other along the vertical direction of (010) plane via the Zn-O-P bonds displaced by +1/2 in the [001] direction to form the three-dimensional framework of $CoZnPO_4$-I (Fig.7c). Each 10-ring is blocked by double 4- and 6-rings around it. So the tendency to construct 10-ring channels is interdicted with only clathrate $6^9 4^6$ cages to be formed.

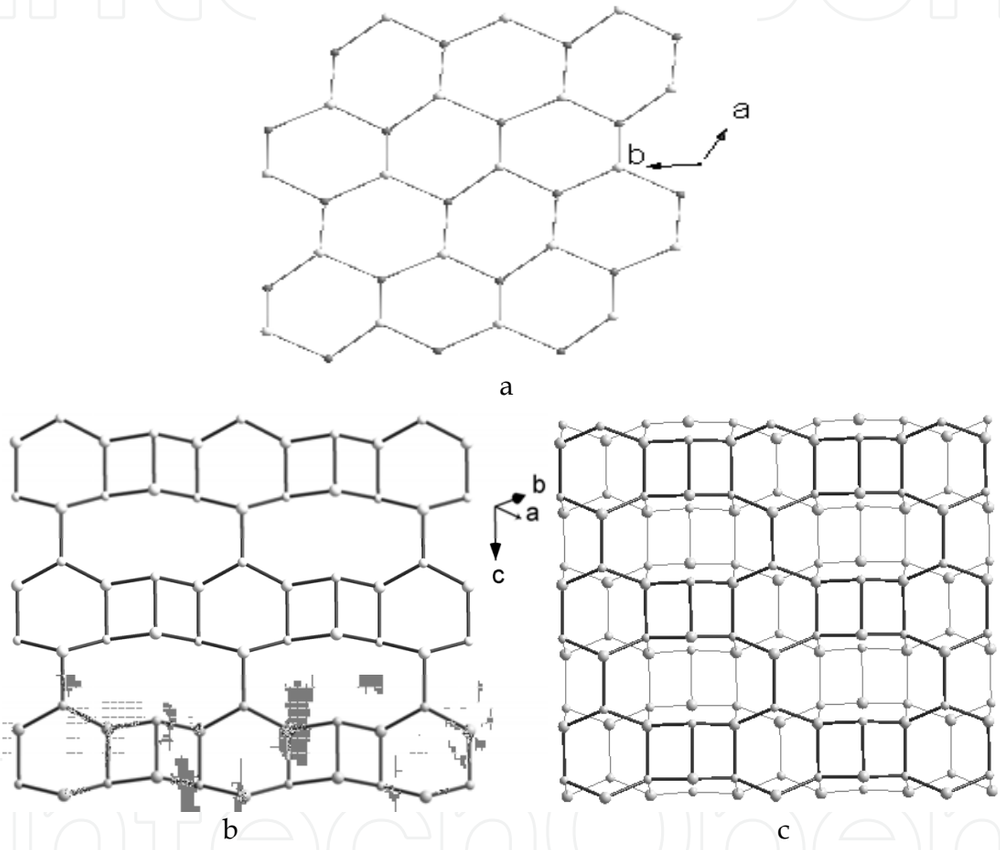


Fig. 7. (a) The crystal structure of $CoZnPO_4$-I consisted of 6-rings viewed down [001]; (b) A sheet extends along the (010) plane consisted of 4-, 6-, and 10-rings;(c) The sheets stacked along the direction vertical to the (010) plane (each node is a T-atom, oxygen atoms are omitted for clarity).

$CoZnPO_4$-II and -III are isostructural with DTF topology and $C_6N_4H_{22}Co_7(PO_4)_6$, respectively. $CoZnPO_4$-II crystallizes in the tetragonal system, space group $P4_2bc$ (No. 106), with $a = b = 14.694(2)$ Å, $c = 8.936(2)$ Å, $\alpha = \beta = \lambda = 90°$, $V = 1929.4(6)$ Å^3, and $z = 8$. $CoZnPO_4$-III crystallizes in the trigonal system, space group $R\bar{3}$ (No. 148), with $a = b = 13.5393(8)$ Å, $c = 15.0443(10)$ Å, $\alpha = \beta = 90°$, $\lambda = 120$ °, $V = 2388.3(3)$ Å^3, and $z = 3$. The three-dimensional framework of $CoZnPO_4$-II can be described as the stacking of 4.8^2 nets along the [001] direction connecting through the UUDDUUDD linkages of each tetrahedral atom around

the 8-ring channels with protonated ethylenediame cations accommodated in the 8-ring channel (Fig.8).

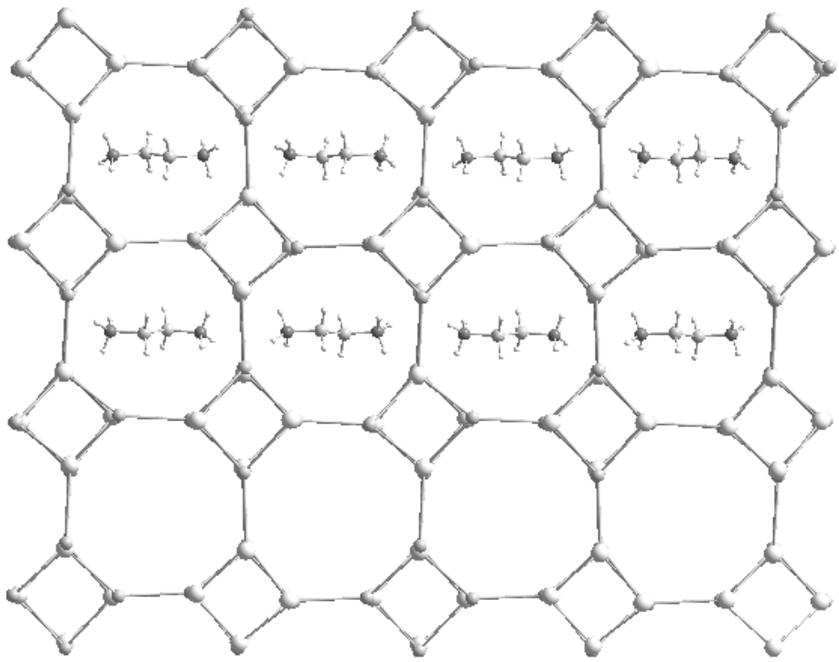


Fig. 8. $CoZnPO_4$-II seen along [001] direction showing the stacked 4.8^2 nets to form 3D framework and 8-ring with diprotonated ethylenediame cations accommodated in the channel (each node is a T-atom, oxygen atoms are omitted for clarity).

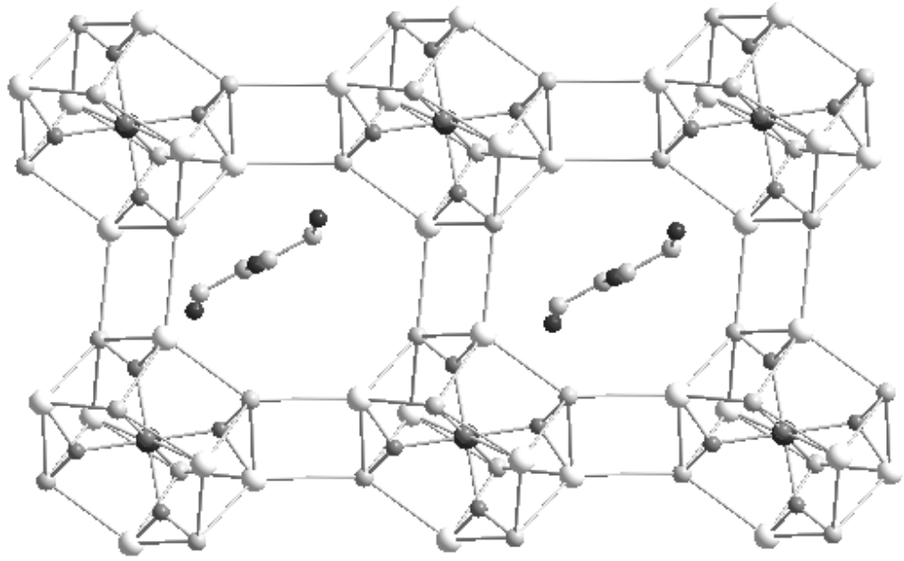


Fig. 9. $CoZnPO_4$-III I seen along [100] direction showing the 8-ring channels with diethylenetriaminum cations accommodated in the channel.

$CoZnPO_4$-III possesses a three-dimensional architecture similar to $C_6N_4H_{22}Co_7(PO_4)_6$, but with the composition of $[C_4N_3H_{16}]_{1.33}[Co_{2.41}Zn_{3.59}(PO_4)_6]$. Its structure is made of CoO_6, ZnO_4 (or CoO_4), and PO_4 polyhedra. The cobalt octahedron is surrounded by six zinc tetrahedra to form the CoZn(or Co)$_6O_6$ cluster which are linked via six PO_4 tetrahedra to other clusters to form its framework. The clusters are arranged in such a manner that each cluster is displaced by half its *a*-distance from its neighbors, forming a honeycomb layer. The next layer of clusters is identical to the first but is displaced along the *a*-axis by half the unit cell so that the honeycomb channels are capped. The framework of AB-type stacking results in the formation of 8-ring channels at an angle to *a*-axis (Fig. 9).

4. The in situ framework transformation of cobalt-zinc phosphates in the presence of linear polyamines

Although linear polyamines cannot decompose at low crystallization temperature, experiments have shown the crystallization time also affects the crystal structure transformation. Another typical result that we have found is the transformation of two cobalt-zinc phosphates, $CoZnPO_4$-VI and $CoZnPO_4$-VII. $CoZnPO_4$-VI was synthesized by using TETA as the template, which can be transformed into $CoZnPO_4$- VII with the increase of crystallization time in 140°C.

4.1 Synthesis and initial characterization

$CoZnPO_4$-VI and $CoZnPO_4$-VII were synthesized hydrothermally from a mixture of ZnO, $2CoCO_3 \cdot 3Co(OH)_2 \cdot H_2O$ (47.5%), H_3PO_4 (85%), TETA, HF (40%), H_2O with a typical molar ratio being $2.4ZnO:0.6CoO:4H_3PO_4:2TETA:4HF:400H_2O$, and the experiment was similar to the previous synthesis. When the crystallization period was 4.5 days, prevailingly light blue sheet-like crystals (named $CoZnPO_4$-VI) and a less number of dark blue block crystals (named $CoZnPO_4$-VII) can be obtained. When the crystallization period was extended to 15 days, sheet-like crystals become significantly fewer and block crystals increase. It can be seen that $CoZnPO_4$-VI can be gradually transformed into $CoZnPO_4$-VII with the increase of crystallization time.

Scanning electron micrograph (SEM) image (Fig.10) shows the morphology of $CoZnPO_4$-VII is as a relatively large irregular block, it is distinct from $CoZnPO_4$-VI (Fig.1c). XRD patterns of $CoZnPO_4$-VI and $CoZnPO_4$-VII have also shown they are two distinguishing phases with different diffraction peaks (Fig.10 and Fig.1c).

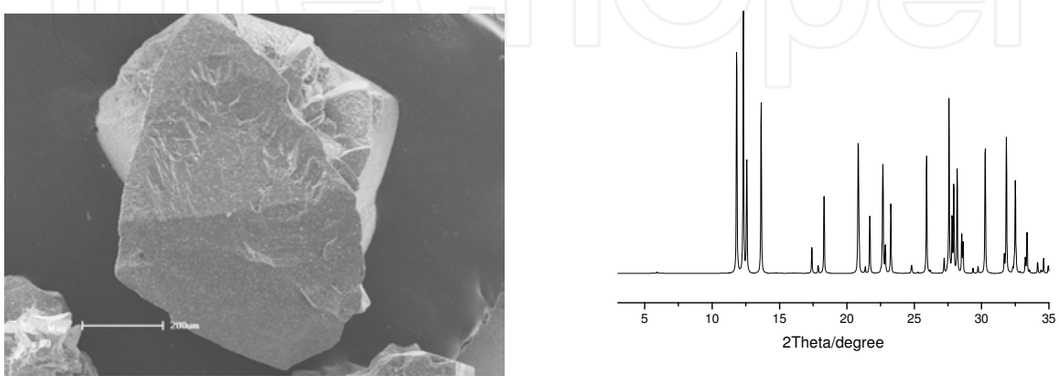


Fig. 10. SEM image and XRD pattern of $CoZnPO_4$-VII.

4.2 Crystal structure of $CoZnPO_4$-VII

Single crystal analysis and Inductively Coupled Plasma atomic emission spectroscopy (ICP) analysis reveal that $CoZnPO_4$-VII is composed of $C_6H_{22}Co_0N_4O_{16}P_4Zn_4$; it crystallizes in the triclinic system, space group $P\bar{1}$ (No. 2), with a = 8.0871(16) Å, b = 8.4237(17) Å, c = 14.961(3) Å, α =89.57(3)°, β = 88.29(3)°, γ =76.23(3)°, V = 989.4(3) Å^3, and z = 2.

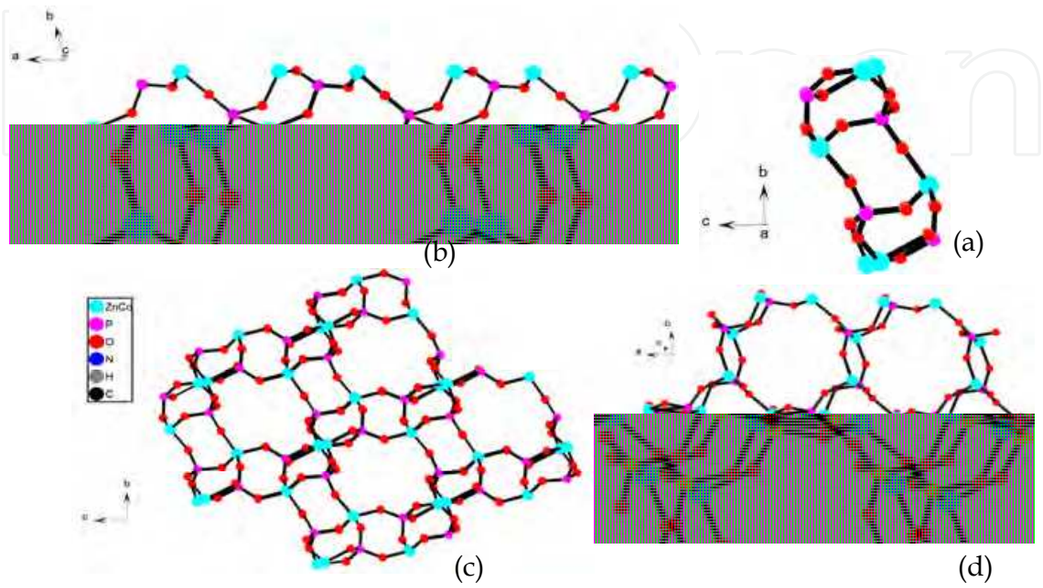
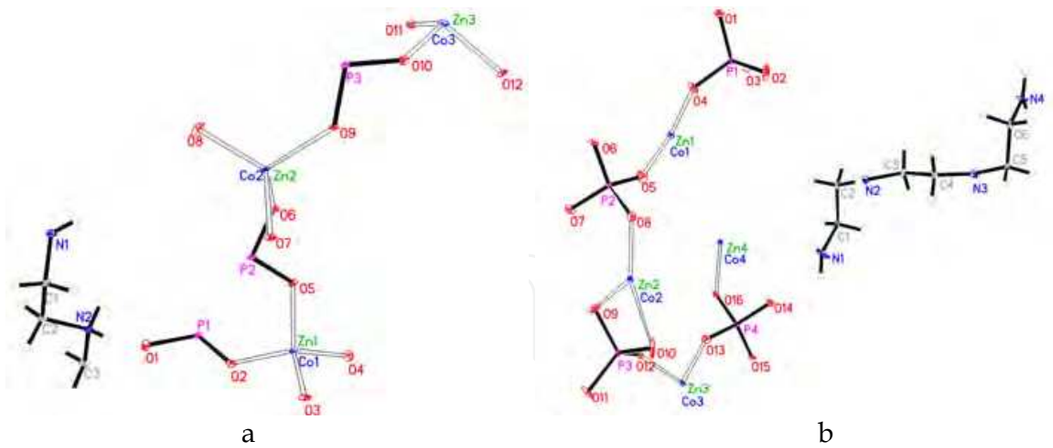


Fig. 11. (a) SUB-c; (b) SUB-c along a-axis; (c) Structure of 8-rings along a-axis; (d) Structure of 8-rings along c-axis.

The biggest feature in the structure of $CoZnPO_4$-VII is that there are two cross-linked 8-ring channels in the structure. The three-dimensional framework of $CoZnPO_4$-VII can be also described as the stack of a secondary structural unit (SBU-c) (Fig.11a). In the direction of a-axis, the connection of 8-rings by three 4-rings forms a ladder (SBU-c) (Fig.11b); in the direction of b-axis ladders are joined by sharing edges, spreading the layers running ab-plane. Then adjacent layers are connected with 4-rings. All described above spread the three-dimensional framework of $CoZnPO_4$-VII and exhibit a 8-ring channel system running along the direction of a-axis (Fig.11c). The arms of channels are constituted mainly by SBU-c. At the same time they form another 8-ring channel system running the direction of c-axis (Fig.11d).

4.3 Relationship between $CoZnPO_4$-VI and $CoZnPO_4$-VII

The similarities between $CoZnPO_4$-VI and $CoZnPO_4$-VII provide the possibility of transformation. On one hand, both of them are composed of Co,Zn,P,O elements, and all Zn (Co) atoms and P atoms in their structures are tetrahedrally coordinated by oxygens, which have been seen from their asymmetric unit structures (Fig.12). On the other hand, the templates filled in their inorganic frameworks are TETA, and both of them crystallize in the triclinic system, space group $P\bar{1}$ (No. 2). All of these result in the transformation of $CoZnPO_4$-VI and $CoZnPO_4$-VII with the increase of crystallization time.



a b

Fig. 12. The asymmetric unit structures of two compounds (a) $CoZnPO_4$-VI; (b)$CoZnPO_4$-VII.

5. Investigation of the in situ decomposition of linear polyamines during hydrothermal synthesis of cobalt-zinc phosphates

In this section, polyamines such as diethylenetriamine, triethylenetetramine, and tetraethylenepentamine were used as structure directing agents to investigate the in situ decomposition of linear polyamines during the crystallization of microporous zinc-cobalt phosphate materials. Mixtures of water and ethylene glycol were used as solvents. Monoamines, such as n-propylamine, n-butylamine, n-dipropylamine, n-tripropylamine and ethanolamine were used as assistant amines.

5.1 Experimental methods

The important basis for determination of polyamines' decomposition is consideration of the template molecules in the framework of all crystals. From the summarized above, we know that the template molecules in the framework of $CoZnPO_4$-I, $CoZnPO_4$-II, $CoZnPO_4$-III, $CoZnPO_4$-IV, $CoZnPO_4$-V and $CoZnPO_4$-VI are NH_4^+, en, DETA, DETA, DETA and TETA, respectively (Fig.13).

Previous studies have shown preliminary that temperature is an important factor for controlling the hydrolysis of linear polyamines. Other, the addition of different assistant templates has different effects on decomposition of propylamines while using the straight-chain polyamines as a precursor of the template in the synthesis of cobalt-zinc phosphates. In order to investigate the decomposition of polyamines, the same ratio of gel should react for a certain time at different temperatures, and the pH value of gel should be adjusted to pH (7.0-9.0) by the addition of different assistant templates. The selected molar ratio of gel is $2ZnAc_2 \bullet 2H_2O$:$1CoAc_2 \bullet 4H_2O$:9.6EG:10.5H_3PO_4:95.4H_2O:1.8R (R is DETA, TETA, TEPA respectively).

5.2 Discussions of factors affecting decomposition of polyamine

The results are shown in Table. 2 when crystallizing at different temperatures for 6 days.

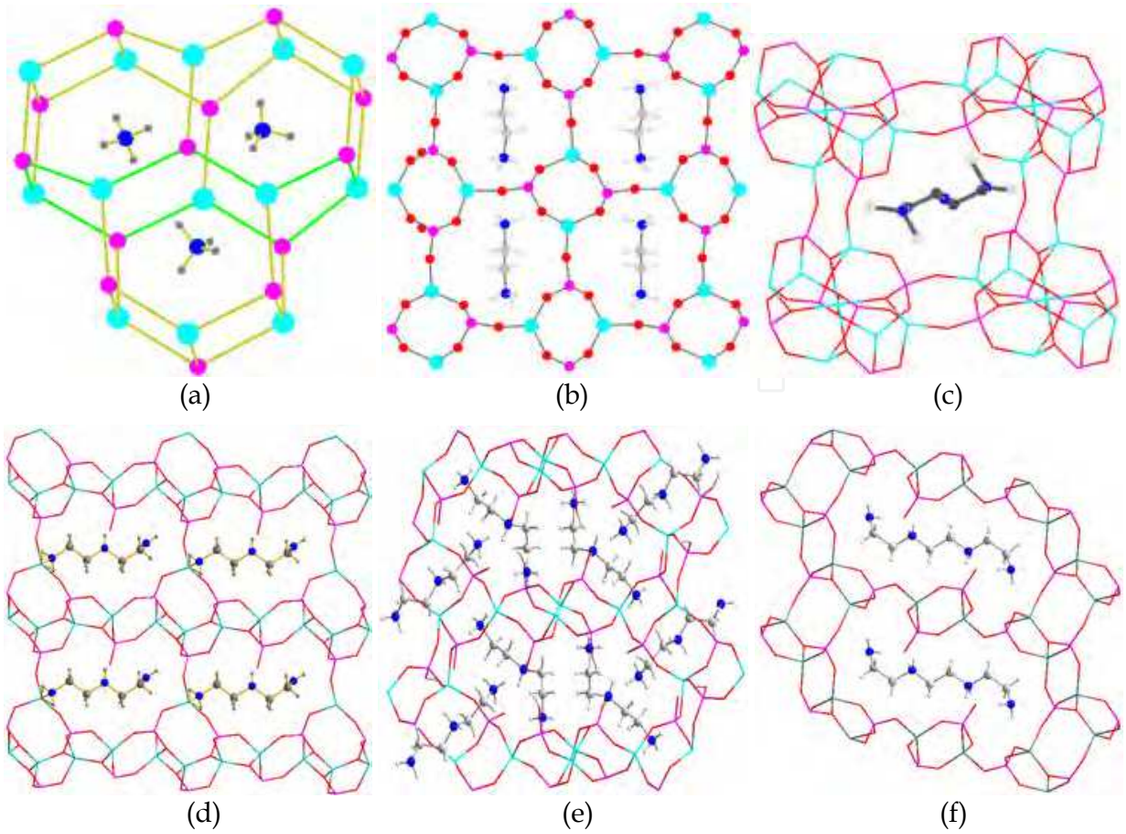


Fig. 13. The structures of six compounds:(a) $CoZnPO_4$-I;(b) $CoZnPO_4$-II;(c) $CoZnPO_4$-III; (d) $CoZnPO_4$-IV;(e) $CoZnPO_4$-V;(f) $CoZnPO_4$-VI.

5.2.1 Temperature effect on decomposition of polyamines

From Table.2, it can be found that high temperature favors the hydrolysis of linear polyamines, prior to adding the same case of secondary amines (*n*-propylamine). For DETA, it is special that it can be decomposed completely into NH_4^+ in 200 °C, still partially decomposed. It is decomposed completely into en in 180 °C, and cannot break down in 160 °C. For TETA, it can be decomposed completely into DETA in 200 °C, and can not break down lower than 160 °C. For TEPA, it also can be decomposed completely into NH_4^+ in 200 °C, and decomposed completely into DETA in 180 °C and 160 °C. Therefore, pure phase is easy to be synthesizes at low temperature.

5.2.2 Assistant template on decomposition of polyamines

We only study the products synthesized at the temperature of 200°C. In the present investigation when crystallizing the mixture of 2:1:9.6:10.5:95.4:1.8 $ZnAc_2$:$CoAc_2$:EG:H_3PO_4:H_2O:DETA at 200 °C for 6 days (assistant amines have not been added), only the pure phase of $CoZnPO_4$-I has been obtained with only ammonium in the structure. It means the complete decomposition of DETA. Meanwhile, the case using triethylenetetramine or tetraethylenepentamine as the SDA also gives the same results, namely, crystallizing at 200 °C has also resulted in the formation of $CoZnPO_4$-I as the only product

However, when an assistant amine, such as *n*-propylamine, was added to the mixture to increase the pH value to 7–9, even if the mixture is crystallized at 200 °C, three metal phosphates ($CoZnPO_4$-I, -II, -III) have been obtained with diethylenetriamine still encapsulated in the pores of $CoZnPO_4$-III. It indicates that the presence of *n*-propylamine can restrain the hydrolysis of diethylenetriamine during the crystallization. It can be found from Table 2 that, apart from *n*-propylamine, other assistant amines, such as *n*-butylamine, dipropylamine, and tripropylamine, can also restrain the decomposition of diethylenetriamine to some extent. The influence of second organic amine may be attributed to the effect of the pH on hydrolysis of the linear polyamines. In the case of triethylenetetramine or tetraethylenepentamine, the controlling effects of assistant amine are less prominent than for diethylenetriamine. $CoZnPO_4$-II and -III have only been obtained as the pure phases by varying assistant amine or crystallizing temperature.

$CoZnPO_4$	-I	-II	-III	-IV	-V	-VI
Diethylenetriamine (Crystallizing at 200 °C)						
without assistant amine	y	n	n	N	n	N
n-propylamine	y	y	y	N	n	N
n-propylamine(180 °C)	n	y	n	N	n	N
n-propylamine(160 °C)	n	n	y	N	n	N
n-butylamine	y	y	n	N	n	N
dipropylamine	y	y	y	Y	n	N
tripropylamine	n	y	n	N	n	N
Triethylenetetramine (Crystallizing at 200 °C)						
without assistant amine	y	n	n	N	n	N
n-propylamine	n	n	y	Y	n	N
n-propylamine(160 °C)	n	n	n	Y	n	Y
n-propylamine(140 °C)	n	n	n	N	n	Y
Tetraethylenepentamine (Crystallizing at 200 °C)						
without assistant amine	y	n	n	N	n	N
n-propylamine	y	n	n	N	n	N
n-propylamine(180 °C)	n	n	y	N	n	N
n-propylamine(160 °C)	n	n	y	N	n	N

[a] The reacting mixture with the molar ratio of 2:1:9.6:10.5:95.4:1.8 $ZnAc_2$:$CoAc_2$:EG:H_3PO_4:H_2O:R was crystallized for 6 days; y = yes, compound has been obtained; n = no,compound has not been obtained.

Table 2. Products obtained by adding various assistant amines to adjust the pH value of the mixture to 7-9[a]

6. Conclusions

Synthesis of zinc-cobalt phosphate materials have been investigated by using linear polyamines, such as tetraethylene-pentamine, triethylenetetramine or diethylenetriamine as SDA. During the investigation of decomposition of polyamines seven cobalt-substituted zinc phosphates were obtained: $CoZnPO_4$-I-VII.

$CoZnPO_4$-I, $CoZnPO_4$-II, and $CoZnPO_4$-III, have been synthesized from a single gel at 200 °C in the presence of diethylenetriamine as the structure-directing agent. Structural analysis reveals that species encapsulated in the structures of $CoZnPO_4$-I, $CoZnPO_4$-II, and

$CoZnPO_4$-III are ammonium, ethylenediaminum, and diethylenetriaminum, respectively, which can be attributed to the partly in situ decomposition of diethylenetriamine molecules during the crystallization procedure. $CoZnPO_4$-IV, $CoZnPO_4$-V and $CoZnPO_4$-VI with differently unique 3D framework topologies have been synthesized under hydrothermal or solvothermal conditions in the presence of linear polyamines as structure directing agents (SDA). $CoZnPO_4$-VI and $CoZnPO_4$-VII, which were synthesized by using TETA as the template, are symbiotic and $CoZnPO_4$-VI can be transformed into $CoZnPO_4$-VII with the increase of crystallization time in 140°C.

In the synthesis of zinc-cobalt phosphates, temperature is an important factor, favoring the hydrolysis of linear polyamines at higher temperature. Investigations have also found that the in situ decomposition of tetraethylene-pentamine, triethylenetetramine, or diethylenetriamine can be controlled by using second organic amines, such as propylamine as the assistant organic additive. The presence of an assistant amine can restrain the hydrolysis of diethylenetriamine during the crystallization. If synthesis conditions can be controlled, different structures can be transformed into each other.

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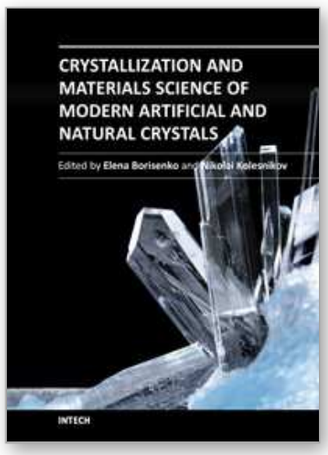

Crystallization and Materials Science of Modern Artificial and Natural Crystals

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