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Journal of Solid State Chemistry 177 (2004) 3229–3234

JOURNAL OF SOLID STATE CHEMISTRY

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Rapid Communication

$Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$: a purely inorganic open-framework zincophosphite with octahedral zinc complex $[Zn(H_2O)_6]^{2+}$ encapsulating in the channels

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Received 2 February 2004; received in revised form 14 April 2004; accepted 19 April 2004

Abstract

The hydrothermal synthesis and single crystal structure of $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$ are reported. The structure is built-up from vertex linking ZnO_4 tetrahedral and HPO_3 pseudo-pyramids units, giving rise to a three-dimensional framework with large 8, 16-membered ring channels. The zincophosphite is purly inorganic with the octahedral zinc complex filled in the channel. The synthesis of system required the presence of the organic amine which is not incorporated into the structure of the product. The framework-metal complex encapsulating in the channel is the first time appeared in open-framework zincophospates and zincophosphites. Crystal data: $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$, $M = 689.52$, orthorhombic, *Fddd* (No. 70), $a = 9.679(4)$ Å, $b = 11.926(5)$ Å, $c = 30.691(12)$ Å, $V = 3543(2)$ Å^3, $Z = 8$, $\rho_{cacl} = 2.585\,Mg/m^3$, $\mu = 5.798\,cm^{-1}$, $R = 0.0265$, $R_w = 0.0406$.

Keywords: Hydrothermal synthesis; Single crystal; Three-dimensional; Zincophosphite; Inorganic

1. Introduction

Open-framework metal phosphates have received much attention during the last decade due to their rich structural chemistry and potential applications in catalysis, separation and ion-exchange processes [1]. One of the main goals of this research is to explore microporous materials with large ring size. Since the 18-membered ring material VPI-5 [2] appeared, the extra-large 20- and 24-membered ring open-framework materials [3,4] have been prepared. The structural diversity of open-framework zincophosphates is especially eye-catching. Since the first microporous zincophosphates has been reported by Gier and Stucky [5], more than 120 novel structures have been synthesized by changing the structure-directing agents [6]. In pursuit of novel open-framework structures, the diversity of the organic species was paid much attention to than the $[PO_4]^{3-}$ phosphate anion. It is interesting that the pseudo-pyramidal $[HPO_3]^{2-}$ is structurally similar to the $[PO_4]^{3-}$ phosphate anion. It might be anticipated that pseudo-pyramidal $[HPO_3]^{2-}$ can group into open-framework structure with TOs polyhedral. With the changing of the templates, more than 10 kinds of zincophosphites have been synthesized [7–16]. Some structures of these zincophosphites are quite typical, such as Zn–N (zinc-to-template) bonds [11], polyhedral 12-member ring [12] and polyhedral 16-ring windows [13,14].

To data, extra large number of organic zincophosphates and zincophosphites have been synthesized and characterized by changing the organic directing agents. However, the occurrence of the purely inorganic zincophosphates and zincophosphites is particular rare compared to the organically templated phases. Only a small number of the ZnPO's are aware of having the purely inorganic composition. For instance, a zincophosphate of formular $H[Zn_4(PO_4)_3]H_2O$ with one six-ring channel and one eight-ring channel [17], the zincophosphate $Zn_2(OH)PO_4$ forming adamite-type $M_2(OH)XO_4$ structure [18], the zincophosphites $Zn(H_2PO_3) \cdot 3H_2O$

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doi:10.1016/j.jssc.2004.04.060

and $Zn_2(HPO_3)(H_2O)_4 \cdot H_2O$ with octahedral zinc in the framework [19], zincophosphite $Zn_{11}(HPO_3)_8(OH)_6$ presenting a isotypical with $A_3Te_2O_6(OH)_2$ ($A = Co$, Ni) [20].

The metal organic complex have been explored to serve as the templating agents in zincophosphate containing $[Co(en)_3]_2[Zn_6P_8O_{32}H_8]$, $[Co(en)_3][Zn_8P_6O_{24}Cl] \cdot H_2O$ [21] and $[\{Zn_2(HPO_4)_4\}\{Co(dien)_2\}] \cdot H_3O$ [22]. In their synthesis system the addition of the metal complex as the starting materials are necessary for the crystalline reaction products and the metal in the channel is also different to the metal in the framework. In this paper we report the synthesis and crystal structure of a purely inorganic zincophosphite with the framework-metal complex encapsulating in the channel.

2. Experimental section

2.1. Synthesis

The $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$ was synthesized hydrothermally under autogenous pressure with *n*-tripropylamine (TPA) as a structure directing agent. A total of 0.81 g ZnO, 0.82 g H_3PO_3, 2.86 ml TPA (molar ratio of Zn:P:TPA = 1.0:1.0:1.5) and 18 ml H_2O were added to a PTFE beaker and shaken well. The initial pH of the supernatant liquid was 6. The mixture was transferred to a stainless steel autoclave. Subsequently, the autoclave was installed in a 90°C oven for 4 days. The pH of the system still was 6 at the time of opening the autoclave. The large, transparent, faced crystal was filtered and washed with deionized water and dried at 60°C. After a series of experiments, we found that the title compound can be synthesized at molar ratio of Zn:P:TPA = 1.0:1.0:1.3–1.7.

2.2. Initial characterization

The powder XRD pattern of $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$ was collected using a RigakudMax-2500 diffractometer with a monochromated Cu$K\alpha$ X-ray source (step size of 0.01°, count time = 4 s, 2θ range = 5–35°). TG/DTA data was collected on the Rigaku Standard Type TG-DTA Analyzer (ramp rate 20°C/min in flowing air). Infrared absorption spectra were obtained on a Bruker Vector 22 FT-IR spectrometer (with KBr wafers).

2.3. Crystal structural determination

A suitable single crystal ($0.08 \times 0.04 \times 0.04\,mm^3$) of the compound was carefully selected under a microscope and glued to a thin glass fiber with superglue adhesive. The X-ray diffraction intensity data was collected on a Bruker SMART 1000 CCD diffractometer with monochromated Mo$K\alpha$ ($\lambda = 0.71073$ Å) radiation at room temperature. The final unit cell parameters were determined by a least-squares fit of 3960 reflections in θ ranges of 2.65–26.33°. The structure was solved by direct methods and refined based on $|F|^2$ by full-matrix least-squares method (SHELXTL97 program system [23]). Crystallographic data for the compound are listed in Table 1.

Table 1
Crystallographic data for $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$

Empirical formula	$Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$
Formula mass	689.52
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Fddd* (No. 70)
a (Å)	9.679(4)
b (Å)	11.926(5)
c (Å)	30.691(12)
V (Å)^3	3543(2)
Z	8
Calculated density ($mg\,m^{-3}$)	2.585
Absorption coefficient (mm^{-1})	5.798
F(000)	2720
Crystal size (mm^3)	$0.08 \times 0.04 \times 0.04$
Reflections collected/unique	3960/917 [R(int) = 0.0377]
Data/restraints/parameter	917/0/64
Goodness-of-fit on F^2	0.997
Final R indices [$I > 2\sigma(I)$]*	$R1 = 0.0265$, w$R2 = 0.0625$
R indices (all data)	$R1 = 0.0406$, w$R2 = 0.0671$
Largest diff. peak and hole (Å^{-3})	0.595 and $-0.424e$

Note: $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD_413095.

3. Result and discussion

The power XRD pattern is entirely consistent with the simulated one based on the structure determined by single-crystal X-ray diffraction, as shown in Fig. 1, which suggested the phase purity of the as-synthesized samples. The TG-DTA pattern (Fig. 2) shows a continuous weight loss of 14.7% at the range of 17–300°C attributing to the removal of H_2O in the product, which is approximately in agreement with the result by calculation. The three exothermic picks and the continuous weight uptake over the temperature range ~300–800°C correspond to aerial oxidation of phosphite to phosphate. The phase recrystallizes to β-$Zn_2P_2O_7$ (JCPDS: 11-0026), which was confirmed by powder X-ray diffraction pattern of calcining the sample

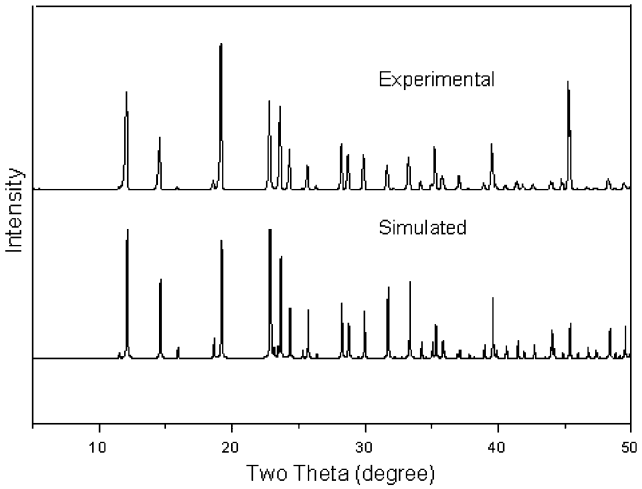

Fig. 1. Simulated and experimental power X-ray diffraction patterns of $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$.

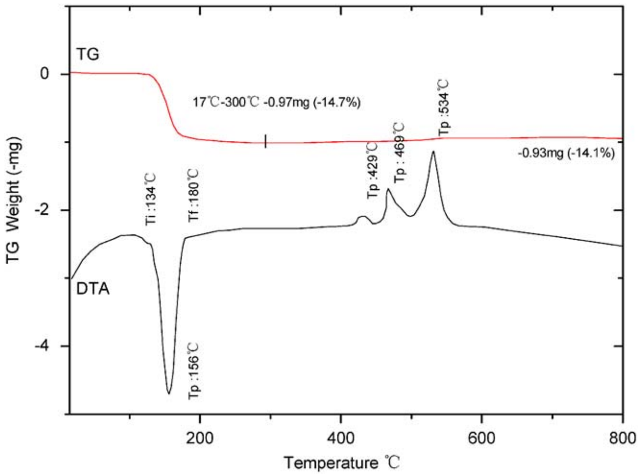

Fig. 2. TG-DTA curves of $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$.

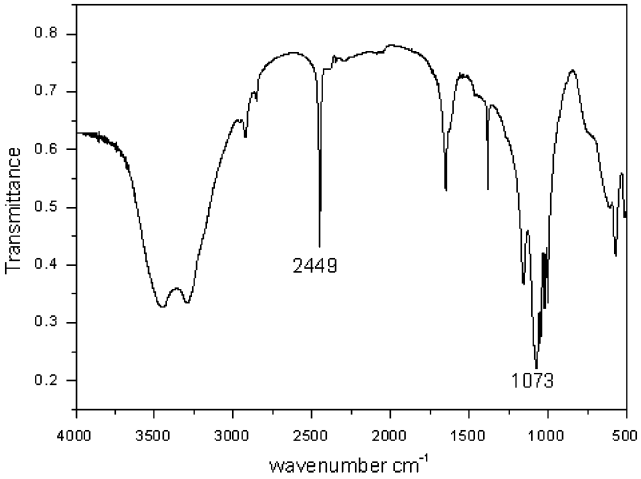

Fig. 3. IR spectra of $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$.

at 650°C for 2 h and the phase keeps stable up to 800°C. FT-IR spectra of $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$ in Fig. 3 show a strong vibration at about 2449 cm^{-1}. The frequency is characteristic of P–H stretching and indicates the existence of only one environment for the phosphite group. The vibrations seen in 1000–1200 cm^{-1} ascribe to the PO_3 group or hydrogen bonded PO_3 group [24].

In the single crystal structure of $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$, the asymmetric unit contains nine non-hydrogen atoms, of which six belong to the framework and three to the channel filler (Fig. 4). The framework is built up from alternating ZnO_4 tetrahedral and HPO_3 pseudo-pyramids, sharing vertices, as Zn–O–P bonds. Both Zn1 and Zn2 make four links to nearby P atoms [d_{av}(Zn1–O) = 1.940(2) Å, d_{av}(Zn2–O) = 1.955(2) Å] and P1 make three P–O–Zn links [d_{av}(P–O) = 1.515(2) Å]. The O1, O2 and O3 atoms serves as bicoordinate Zn–O–P bridges, with an average bond angle of 129.49° (spread of values 125.91–133.69). These geometrical parameters are in good agreement with those reported for similar compound in the literature [7–16]. All these P species make three links to zinc neighbors via O atoms and are presumed to posses the characteristic $[HPO_3]^{2-}$ terminal P–H bond. There is no terminal P–O and P–OH bonds, which usual occur in templated zinc phosphates. Select geometrical data are listed in Tables 2 and 3.

The average bond length of Zn(3)–O4 is 2.026(2) Å and shorter than the bond of Zn(3)–O5, the length of which is 2.197(3) Å. The Zn(3) connecting with six water molecules is octahedral and acts as the channel filler. The zinc's geometrical parameters of the $[Zn(H_2O)_6]^{2+}$ are similar to the octahedral coordinated zinc which has been founded only in the framework of zincophosphites [19] and zincophosphates [25]. The framework structure of $Zn_3(HPO_3)_4$ would result in a net framework charge of −2. The presence of $[Zn(H_2O)_6]^{2+}$ would account for the total charge needed for the charge balance. The hexaaquozinc ion interacts with the framework through O–H···O hydrogen bonds to stabilization the whole architecture with the distances range from 2.718 to 2.927 Å. The detail geometries of the hydrogen bonds are listed in Table 4.

In $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$, the polyhedral building blocks combine to yield an extended network with three-dimensional character. In the structure the zinc atoms show two different coordination forms, one is tetrahedrally coordinated and the other is octahedrally coordinated. The tetrahedrally coordinated zinc acts as the build-up of the network, the encapsulated octahedrally coordinated zinc in the channels balance the charge of the framework. When viewed down [0 1 0], an 8-ring channel appeared, the atom–atom size of which is 7.68 × 8.64 Å (Fig. 5). The elliptical 16-ring is built up from eight ZnO_4 and eight HPO_3 along $[\bar{2}30]$ (Fig. 6: atom–atom dimensions ∼14.45 × 4.29 Å). Two $[Zn(H_2O)_6]^{2+}$ cations occupy each elliptical 16-ring and

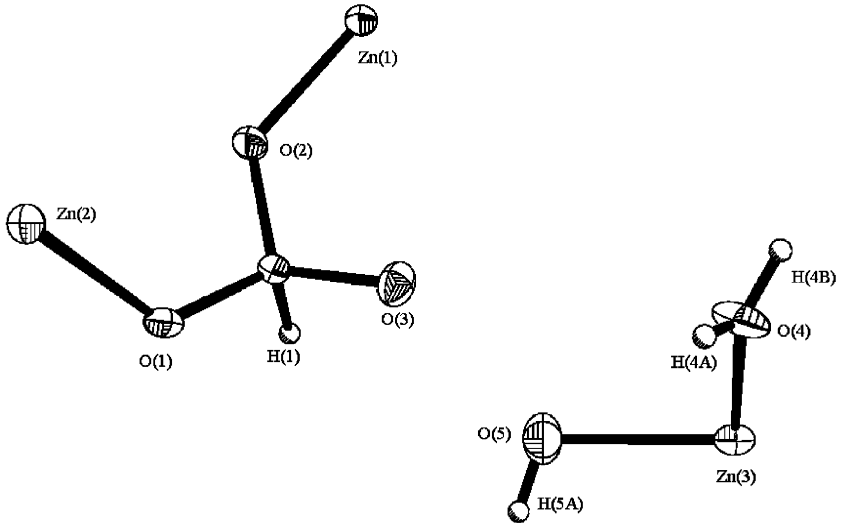

Fig. 4. Fragment of the $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$ structure showing the atom labeling scheme.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$

	X	*Y*	*z*	U_{eq}
Zn(1)	−1250	8750	2269(1)	15(1)
Zn(2)	1250	6250	1250	19(1)
Zn(3)	3750	8750	3750	18(1)
P(1)	1728(1)	8017(1)	1977(1)	14(1)
O(1)	2318(2)	7237(2)	1631(1)	20(1)
O(2)	251(2)	8345(2)	1871(1)	20(1)
O(3)	1894(3)	7573(2)	2436(1)	21(1)
O(4)	2286(2)	7539(2)	3717(1)	27(1)
O(5)	3750	8750	3034(1)	32(1)

Table 3
Selected geometrical data for $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$

Zn(1)–O(3)#1	1.922(2)	Zn(1)–O(3)#2	1.922(2)
Zn(1)–O(2)#3	1.959(2)	Zn(1)–O(2)	1.959(2)
Zn(2)–O(1)	1.954(2)	Zn(2)–O(1)#4	1.955(2)
Zn(2)–O(1)#5	1.955(2)	Zn(2)–O(1)#6	1.955(2)
Zn(3)–O(4)#7	2.026(2)	Zn(3)–O(4)	2.026(2)
Zn(3)–O(4)#8	2.026(2)	Zn(3)–O(4)#9	2.026(2)
Zn(3)–O(5)#9	2.197(3)	Zn(3)–O(5)	2.197(3)
P(1)–O(2)	1.516(2)	P(1)–O(3)	1.515(3)
P(1)–O(1)	1.523(2)	P(1)–H(1)	1.2605
O(3)–Zn(1)#2	1.922(3)	O(4)–H(4A)	0.8439
O(4)–H(4B)	0.8469	O(5)–H(5A)	0.8790

Symmetry transformations used to generate equivalent atoms: $\#1 x - 1/4, y + 1/4, -z + 1/2$; $\#2 - x, -y + 3/2, -z + 1/2$; $\#3 - x - 1/4, -y + 7/4, z$; $\#4 x, -y + 5/4, -z + 1/4$; $\#7 - x + 3/4, -y + 7/4, z$; $\#8 x, -y + 7/4, -z + 3/4$; $\#9 - x + 3/4, y, -z + 3/4$.

evenly distribute in the channels to balance the framework charge.

The openness of a structure is defined in terms of the tetrahedral atom density [26] (framework density, FD), which is defined as the number if tetrahedral (*T*) atoms per 1000 Å^3. In $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$, the number of the $T (T = \text{Zn, P})$ atoms is 15.8. This indicates that the framework density is quite low. The amount of void the space encapsulated by the framework in $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$ is 758.2 Å^3 (21.4% of the unit cell volume). The unit cell contains no residual solvent

Table 4
Hydrogen bonds for $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	Ang(D–H···A) (°)
O4–H4A···O2 #1	0.84	1.91	2.746(4)	168
O4–H4B···O1#2	0.84	1.89	2.718(3)	166
O5–H5A···O3#3	0.88	2.37	2.927(4)	122

$\#1 x + 1/4, y - 1/4, -z + 1/2$; $\#2 x - 1/4, -y + 3/2, z + 1/4$; $\#3 - x + 3/4, -y + 7/4, z$.

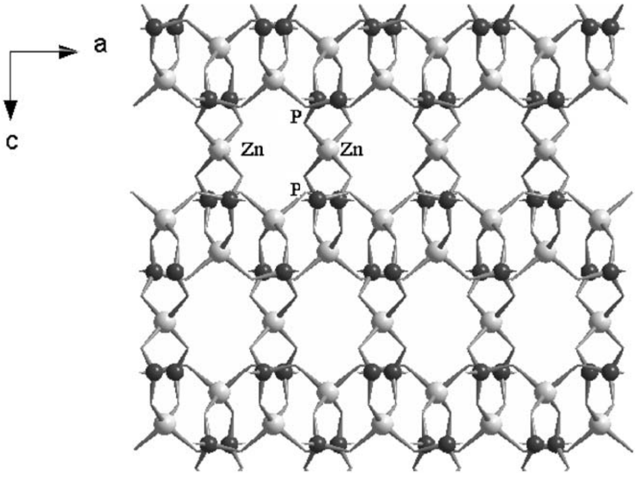

Fig. 5. The channel of $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$ along [0 1 0]. The $Zn(H_2O)_6$ cations were omitted.

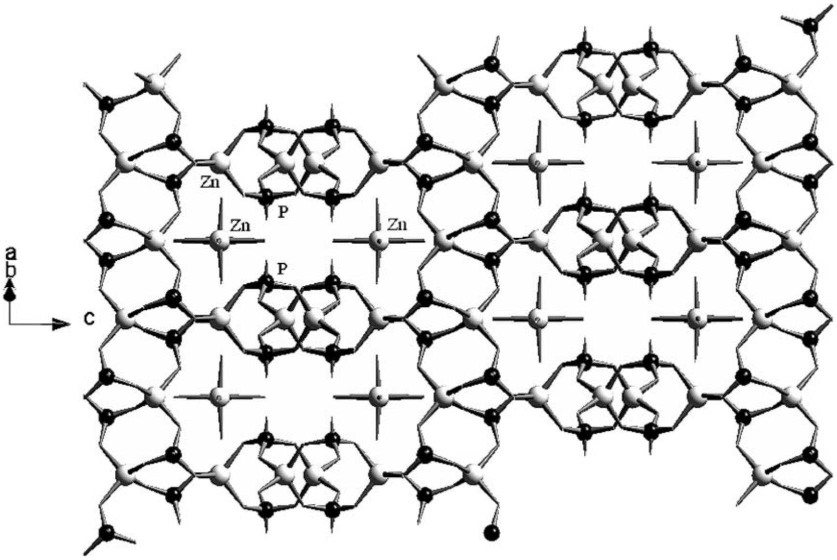

Fig. 6. Viewed approximately down [$\bar{2}30$] of the zincophosphite showing the 16-ring topology. Two $Zn(H_2O)_6$ cations were encapsulated in every 16-ring.

accessible area indicating that the $[Zn(H_2O)_6]^{2+}$ cations essentially fill in the channels.

The calculated weight of all the water species in $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$ is 15.6%, which approximately agrees with the result of the TG experiment (Fig. 1). The result shows that the organic amine TPA does not occur in the channels. This indicates that framework-metal complex $[Zn(H_2O)_6]^{2+}$ is the only channel filler. Framework-metal complex acting as the only channel filler is the first time appeared in the open-framework zincophosphate and zincophosphites, which reveals a novel encapsulating manner in the formation of open-framework materials. The synthesis of the open-framework zincophosphate and zincophosphites required the presence of the organic amine but which is not incorporated into the channel of the product, which has not been reported in the synthesis of zincophosphites before, but similar instances have been reported in the synthesis of the zincphosphate $Zn_2(OH)PO_4$ [18] and $KZn_2(PO_4)(HPO_4)$ [27]. The authors ascribed the possible role of the organic amine to the pH modifier [27]. We also think that playing a modulation role of the TPA to reaction mixture pH is important for the formation of the titled product. However, it may not only be the role, because the phase could not be obtained at the same pH range adjusted by other method. The role of the TPA needs further exploration.

Acknowledgments

We thank China Petroleum & Chemical Corporation (X501024) and the National Natural Science Foundation of China (Grant No. 20233030) for financial support.

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