Hydrothermal Synthesis of New Pure Beryllophosphate Molecular Sieve Phases from Concentrated Amines

Haoyu Zhang,† Minqin Chen,‡ Zhan Shi,§ Xianhui Bu,‖ Yaming Zhou,†
Xin Xu,† and Dongyuan Zhao*,†

*Departments of Chemistry and Analysis and Measurement, Fudan University,
Shanghai, 200433 People's Republic of China, Department of Chemistry, Jilin University,
Changchun, 130023 People's Republic of China, and Department of Chemistry,
University of California, Santa Barbara, California 93106*

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A few new pure beryllophosphate molecular sieves have been hydrothermally synthesized by using concentrated amines such as triethylene tetramine, polyethylene polyamine, piperazine, and pyridine as structure-directing agents. The structures of these compounds were characterized by single-crystal X-ray diffraction. Their structures are similar to the zeolite gmelinite, gismondine, and ABW frameworks, named $BePO_4$−GME, $BePO_4$−GIS, and $BePO_4$−ABW, respectively. $BePO_4$−GME is the first instance of phosphate with GME topology. The organic template was found in the 12-membered ring channels running along [001]; the thermal analysis indicates that the inorganic framework collapses above 400 °C after the removal of the template. $BePO_4$−GIS is a new beryllophosphate, which has three-dimensional, intersecting 8-membered ring channels along the crystallographic [001], [010], and [111] directions. In the concentrated amines system these resulting compounds have similar structural characterizations: Their frameworks that are built up from the connection of BeO_4 and PO_4 tetrahedra all have a 4.8.8 network and can be viewed as built from a different number of cross-linked chains (threes for $BePO_4$−GME and fours for $BePO_4$−GIS and $BePO_4$−ABW). Crystal data for $BePO_4$−GME1: trigonal, space group $P1c$, $a = 13.056(8)$, $b = 13.056(8)$, $c = 9.485(6)$ Å, $V = 1400(2)$ Å^3, $Z = 12$, $R_1 = 0.0513$, $R_w = 0.1519$. Crystal data for $BePO_4$−GIS: monoclinic, space group $C2/c$, $a = 13.514(2)$, $b = 9.0119(10)$, $c = 9.6357(11)$ Å, $\beta = 134.507(2)°$, $V = 836.9(2)$ Å^3, $Z = 4$, $R_1 = 0.0460$, $R_w = 0.1455$. Crystal data for $BePO_4$−ABW: orthorhombic, space group $Pna2_1$, $a = 8.7173(8)$, $b = 8.5889(8)$, $c = 4.9673(5)$ Å, $V = 371.91(6)$ Å^3, $Z = 4$, $R_1 = 0.0304$, $R_w = 0.0805$.

Introduction

Since the discovery of the family of crystalline microporous aluminophosphate in 1982,[1] more extensive research has been devoted to these new types of molecular sieve materials.[2−4] As the framework of $AlPO_4$'s is neutral, attempts to introduce negative charges into the framework by partial substitution of low-valence elements have been made, which results in the cation ions counterbalancing the charges and therefore creating Bronsted acid sites. The materials modified in this manner are potential catalysts both in an oxidation reaction and in an acid-catalyzed reaction.

Many zeolite-type structures based on divalent metal tetrahedral atoms (such as Be^{2+}, Co^{2+}, and Zn^{2+}) have been reported.[5−7] From a structural point of view, beryllium is ideally suited as a building block for a new zeolite structure because its size (0.27 Å) is similar to that of Si^{4+}(0.26 Å) and it has a tendency to have tetrahedral coordination to oxygen atoms.[8] A number of open-framework structures based on beryllium and phosphate have been reported including ABW, ANA, CAN, EDI, FAU, LOS, RHO, BPH, and SOD.[9,10] In addition, some beryllophosphate minerals have been found to possess a zeolite-type framework structure.[11] Unfortunately, among these structures, the majority have small (6- or 8-membered ring) pores, until now only two known zeolite analogues (types FAU and BPH) have a 12-membered ring channel system. Most reported beryllophosphates before are not pure phases. There are no reported examples of an open framework with gmelinite topology in a phosphate system.

Here, we describe a concentrated amine templating method for synthesis of pure phase, large single-crystal

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* To whom correspondence should be addressed.

† Departments of Chemistry and Analysis and Measurement, Fudan University.

‡ Analysis and Measurement, Fudan University.

§ Jilin University.

‖ University of California.

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Table 1. Data of Gel Composition and Hydrothermal Crystallization of Beryllophosphates

sample	pH	temp (K)	time (days)	Na^+/Be	K^+/Be	NH_4^+/Be	products	crystal dimension (μm)
A[a]	10.4	433	8				GME	100−200
B[a]	10.0	453	4				GME	<50
C[a]	9.9	413	15				GME	50−150
D[a]	9.7	433	9				GME	200−400
E[b]	6.6	433	8				GME	200−300
F[a]	9.8	433	8	0.1			GME	<50
G[a]	9.8	433	8		0.1		GME	<50
H[a]	9.7	433	8			0.1	GME	200−400
I[c]	9.3	433	8				GIS	100
J[d]	6.4	433	8				ABW	50−100

[a] Gel of composition, 1:1.25:3.1:95.8 $BeO:P_2O_5:R_1:H_2O$. $R_1 = N(NH_2CH_2CH_2)_3$. [b] Gel of composition, 1:1.25:0.86:97.7 $BeO:P_2O_5:R_2:H_2O$. $R_2 = C_{2n}H_{3+5n}N_{1+n}$ ($n \geq 5$). [c] Gel of composition, 1:1.7:3.14:71.8 $BeO:P_2O_5:R_3:H_2O$. $R_3 = C_4H_{10}N_2{\cdot}6H_2O$. [d] Gel of composition, 1:1.6:54.5:71.8 $BeO:P_2O_5:R_4:H_2O$. $R_4 = C_5H_5N$.

Table 2. Crystal Data and Structure Refinement for $BePO_4$−GME, $BePO_4$−GIS, and $BePO_4$−ABW

	$BePO_4$−GME	$BePO_4$−GIS	$BePO_4$−ABW
formula	$^1/_6(C_6H_{21}N_4)Na_3Be_6P_6O_{24}{\cdot}3H_2O$	$(C_4H_{12}N_2)Be_2P_2O_8$	NH_4BePO_4
formula weight	149.36	296.12	122.02
temperature	293(2) K	293(2) K	293(2) K
wavelength	0.710 73 Å	0.710 73 Å	0.710 73 Å
crystal system	trigonal	monoclinic	orthorhombic
space group	$P\bar{3}1c$	$C2/c$	$Pna2_1$
unit cell dimensions	$a = 13.056(8)$ Å $b = 13.056(8)$ Å $c = 9.485(6)$ Å	$a = 13.514(2)$ Å $b = 9.0119(10)$ Å $c = 9.6357(11)$ Å	$a = 8.7173(8)$ Å $b = 8.5889(8)$ Å $c = 4.9673(5)$ Å
volume, Z	1400.3(15) Å^3, 12	836.9(2) Å^3, 4	371.91(6) Å^3, 4
density (calculated)	2.121 mg/m^3	2.350 mg/m^3	2.179 mg/m^3
adsorption coefficient	0.553 mm^{-1}	0.564 mm^{-1}	0.609 mm^{-1}
$F(000)$	904	1.361	248
crystal size	0.15 × 0.15 × 0.15 mm	0.15 × 0.10 × 0.05 mm	0.15 × 0.05 × 0.05 mm
θ range for data collected	1.80°−23.22°	3.09°−24.99°	3.30°−28.21°
limiting indices	$-14 \leq h \leq 10$ $-3 \leq k \leq 14$ $-7 \leq l \leq 7$	$-17 \leq h \leq 15$ $-11 \leq k \leq 11$ $-12 \leq l \leq 12$	$-8 \leq h \leq 11$ $-11 \leq k \leq 11$ $-5 \leq l \leq 6$
reflections collected	3219	2077	2103
independent reflections	590 [R(int) = 0.0606]	737 [R(int) = 0.0400]	789 [R(int) = 0.0277]
refinement method	full-matrix least-squares on F^2		
data with $I > 2\sigma(I)$/parameter	590/86	737/83	788/64
goodness-of-fit on F^2	1.160	1.149	1.348
final R indices [$I > 2\sigma(I)$][a]	R1 = 0.0486, wR2 = 0.1238	R1 = 0.0460, wR2 = 0.1455	R1 = 0.0304, wR2 = 0.0805
R indices (all data)	R1 = 0.0653, wR2 = 0.1249	R1 = 0.0501, wR2 = 0.1480	R1 = 0.0317, wR2 = 0.0870
largest diff peak and hole	0.262 and −0.289 e Å^{-3}	0.598 and −0.556 e Å^{-3}	0.623 and −0.273 e Å^{-3}

[a] Where $wR2 = [\sum[w(|F_o|^2 - |F_c|^2)^2]/\sum[w(|F_o|^2)^2]]^{1/2}$ and $R1 = \sum||F_o| - |F_c||/S|F_o|$.

beryllophosphates. By using this method, a large pore (12-membered rings) beryllophosphate molecular sieve with the topology isotypic to the gmelinite (denoted as $BePO_4$−GME) has been synthesized for the first time. The channel size is dependent on the size of the amines. When concentrated piperazine and pyridine are used as the templates, a new beryllophosphate structure with a 4.8.8 network similar to gismodnite (denoted as $BePO_4$−GIS) and a known beryllophosphate with ABW topology ($BePO_4$−ABW) are synthesized, respectively.

Experimental Section

Hydrothermal Synthesis. (a) $BePO_4$−GME. Beryllophosphates were hydrothermally synthesized under a concentrated amine system in aqueous media (Table 1). In a typical reaction mixture of composition for $BePO_4$−GME, 0.27 g of $Be(OH)_2$, 1.65 g of 85% H_3PO_4, and 10 g of distilled water were mixed with stirring. Then, 2.74 g of triethylene tetramine and a small amount of NaOH were added until the pH of the mixture was 10.4. After the mixture was stirred at room temperature for 2 h, the resulting synthesis gel composed of 1:1.25:3.1:95.8 $BeO:P_2O_5:R:H_2O$ ($R = N(NH_2CH_2CH_2)_3$) was heated at 160 °C for 8 days in a Teflon-coated steel autoclave. The product was recovered by filtration and washed with deionized water. Polyethylene polyamine [$C_{2n}H_{3+5n}N_{1+n}$ ($n \geq 5$)] instead of triethylene tetramine was used as a structure-directing agent (SDA), according to the above synthesis procedure, the pH value of the final mixture was 6.6, and pure $BePO_4$−GME phase was also obtained.

(b) $BePO_4$−GIS. $BePO_4$−GIS was prepared by mixing $Be(OH)_2$ (0.2 g), 85% H_3PO_4 (0.9 g), and distilled water (6 g). Piperazine hexahydrate (2.8 g) was added to the resulting solution until the pH was 9.3; the mixture composed of 1:1.7:3.14:71.8 $BeO:P_2O_5:R:H_2O$ ($R = C_4H_{10}N_2{\cdot}6H_2O$) was stirred in room temperature for 60 min. The homogeneous gel was then heated at 160 °C for 8 days in a Teflon-coated steel autoclave. The product of a single crystal with a size of 150 × 100 × 50 μm was recovered by filtration and washed with deionized water.

(c) $BePO_4$−ABW. $BePO_4$−ABW was prepared by mixing $Be(OH)_2$ (0.22 g), 85% H_3PO_4 (1.0 g), and distilled water (6 g). Pyridine (20 g) was added to the resulting solution until the pH was 6.4; the mixture composed of 1:1.6:54.5:71.8 $BeO:P_2O_5:R:H_2O$ ($R = C_5H_5N$) was stirred at room temperature for 60 min. The homogeneous gel was then heated at 160 °C for 8 days in a Teflon-coated steel autoclave. The product was recovered by filtration and washed with deionized water.

Characterization. To identify the crystallized phases and to test for phase purity, the X-ray powder diffraction patterns (for both powder and single-crystal samples) were collected before and after calcination on a Rigaku D/Max-IIA diffractometer using Cu Kα radiation. The scanning electron micrographs (SEM) were taken on a Hitachi S-520 electron microscope operating at 20 kV. The elemental analysis was carried out on inductively coupled plasma (ICP) and thermogravimetric analysis/differential thermal analysis (TGA/DTA) were

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\times 10^3$ Å^2) for $BePO_4$−GME1, $BePO_4$−GIS, and $BePO_4$−ABW[a]

	x	*y*	*z*	*U*(eq)
		$BePO_4$−GME1		
P(1)	3311(2)	4436(1)	897(2)	13(1)
Be(1)	4454(7)	3366(8)	−985(10)	16(2)
O(1)	3746(4)	3826(4)	−78(5)	23(1)
O(2)	3278(4)	4008(4)	2393(5)	26(2)
O(3)	2082(4)	4152(4)	396(5)	22(1)
O(4)	4103(4)	5793(4)	835(5)	17(1)
Na(1)	3333	6667	2500	21(2)
Na(2)	3333	6667	−809(6)	42(2)
O(5)	4181(3)	5819(3)	−2500	41(2)
N(1)	10000	0	2500	171(18)
C(1)	8966(6)	1034(6)	2500	77(6)
C(2)	9546(21)	822(18)	1586(26)	68(6)
N(2)	8367(4)	1633(4)	2500	46(3)
		$BePO_4$−GIS		
P(1)	3332(1)	6028(1)	2206(1)	11(1)
O(1)	3251(3)	5695(4)	574(4)	22(1)
O(2)	4656(3)	6862(3)	3896(4)	20(1)
O(3)	2076(3)	6934(3)	1443(5)	24(1)
O(4)	3204(3)	4532(3)	2806(5)	24(1)
Be(1)	3692(5)	6478(6)	−422(7)	11(1)
N(1)	5000	7910(10)	7500	74(3)
C(1)	6803(7)	7568(9)	9361(11)	60(2)
C(2)	4901(8)	9899(9)	9162(12)	64(2)
N(2)	5000	9537(9)	7500	65(3)
		$BePO_4$−ABW		
P(1)	6834(1)	854(1)	8799(5)	9(1)
Be(1)	3258(2)	924(2)	8799(36)	12(1)
O(1)	7355(2)	359(2)	11641(3)	14(1)
O(2)	7324(2)	−425(2)	6805(3)	14(1)
O(3)	7614(2)	2372(1)	8032(4)	17(1)
O(4)	5109(1)	1083(2)	8739(6)	20(1)
N	9953(1)	1916(2)	13746(6)	19(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

performed on a Rigaku PTC-10A analyzer in air with a heating rate of 10 °C/min, from 30 to 1000 °C.

Crystal Structure Determinations. A suitable single crystal of each compound was carefully selected under an optical microscope and glued to a thin glass fiber with epoxy resin. Crystal structure determination by X-ray diffraction was performed on a Bruker AXS SMART 1000 CCD area dectector equipped with a normal-fosus, 2.4-kW sealed-tube X-ray source (Mo Kα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. About 1.3 hemispheres of intensity data were collected at room temperature with a scan width of 0.30° in ω and an exposure time of 30 s per frame. The empirical absorption corrections were based on the equivalent reflections. The structure was solved by direct methods followed by successive difference Fourier methods. All calculations were perform using SHELXTL and SHELXTL-97,[12] and final full-matrix refinements were against F^2. The crystallographic results are summarized in Table 2 and positional coordinates are listed in Table 3 while selected bond distances and angles are given in Table 4.

Results and Discussion

Syntheses. The large single-crystal beryllophosphate $BePO_4$−GME products can be obtained in a concentrated triethylene tetramine solution at 160 °C for 8 days. SEM and optical microscopy images show that $BePO_4$−GME is a pure single-crystal phase (Figure 2a) with a large sharpened hexagonal gyroid morphology (Figure 2b). The large crystal size is around 150 × 150 × 150 μm (Figure 2c). The X-ray powder diffraction reveals that the beryllophosphate product is a pure phase material. Figure 1 showed the powder XRD patterns of beryllophosphate product prepared with concentrated triethylene tetramine. The pattern of the powder sample is similar to a single-crystal pattern (see below), which has relative higher intensity. Both patterns match well with the pattern reported for the GME-type zeolite.[13] This confirms successful synthesis of pure

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $BePO_4$−GME1, $BePO_4$−GIS, and $BePO_4$−ABW

	$BePO_4$−GME1[a]		
P(1)−O(1)	1.504(5)	O(1)−P(1)−O(4)	111.7(3)
P(1)−O(2)	1.517(5)	O(2)−P(1)−O(4)	109.7(3)
P(1)−O(3)	1.531(5)	O(3)−P(1)−O(4)	106.6(2)
P(1)−O(4)	1.543(5)	O(1)−Be(1)−O(2)#1	106.5(5)
Be(1)−O(1)	1.584(10)	O(1)−Be(1)−O(3)#2	108.8(6)
Be(1)−O(2)#1	1.628(11)	O(2)#1−Be(1)−O(3)#2	111.0(6)
Be(1)−O(3)#2	1.633(9)	O(1)−Be(1)−O(4)#3	113.0(6)
Be(1)−O(4)#3	1.646(9)	O(2)#1−Be(1)−O(4)#3	112.3(6)
O(2)−Be(1)#4	1.628(11)	O(3)#2−Be(1)−O(4)#3	105.3(5)
O(3)−Be(1)#5	1.633(9)	P(1)−O(1)−Be(1)	168.7(5)
O(4)−Be(1)#3	1.646(9)	P(1)−O(2)−Be(1)#4	140.2(4)
O(1)−P(1)−O(2)	109.2(3)	P(1)−O(3)−Be(1)#5	134.4(5)
O(1)−P(1)−O(3)	108.0(3)	P(1)−O(4)−Be(1)#3	130.4(4)
O(2)−P(1)−O(3)	111.6(3)		
	$BePO_4$−GIS[b]		
P(1)−O(4)	1.5167(11)	O(4)−P(1)−O(1)	110.2(2)
P(1)−O(3)	1.5184(14)	O(3)−P(1)−O(1)	109.55(12)
P(1)−O(2)	1.540(3)	O(2)−P(1)−O(1)	108.09(9)
P(1)−O(1)	1.543(3)	O(3)#1−Be(1)−O(4)	105.4(2)
Be(1)−O(3)#1	1.614(5)	O(3)#1−Be(1)−O(1)#2	110.1(8)
Be(1)−O(4)	1.620(2)	O(4)−Be(1)−O(1)#2	111.9(6)
Be(1)−O(1)#2	1.628(12)	O(3)#1−Be(1)−O(2)#3	110.2(6)
Be(1)−O(2)#3	1.63(2)	O(4)−Be(1)−O(2)#3	110.4(8)
O(1)−Be(1)#3	1.628(12)	O(1)#2−Be(1)−O(2)#3	108.8(2)
O(2)−Be(1)#2	1.63(2)	P(1)−O(1)−Be(1)#3	133.8(4)
O(3)−Be(1)#4	1.614(5)	P(1)−O(2)−Be(1)#2	133.6(2)
O(4)−P(1)−O(3)	109.13(10)	P(1)−O(3)−Be(1)#4	151.1(5)
O(4)−P(1)−O(2)	110.8(2)	P(1)−O(4)−Be(1)	167.5(2)
O(3)−P(1)−O(2)	109.1(2)		
	$BePO_4$−ABW[c]		
P(1)−O(4)	1.524(3)	O(4)−P(1)−O(3)	105.8(2)
P(1)−O(2)	1.527(3)	O(2)−P(1)−O(3)	109.1(2)
P(1)−O(1)	1.528(3)	O(1)−P(1)−O(3)	110.8(2)
P(1)−O(3)	1.529(3)	P(1)−O(1)−Be(1)	137.8(3)
O(1)−Be(1)	1.606(6)	P(1)−O(2)−Be(1)#1	134.1(3)
O(2)−Be(1)#1	1.632(6)	P(1)−O(3)−Be(1)#2	141.3(3)
O(3)−Be(1)#2	1.632(6)	P(1)−O(4)−Be(1)#3	146.1(3)
O(4)−Be(1)#3	1.612(6)	O(1)−Be(1)−O(4)#4	109.7(3)
Be(1)−O(4)#4	1.612(6)	O(1)−Be(1)−O(3)#2	113.6(3)
Be(1)−O(3)#2	1.632(6)	O(4)#4−Be(1)−O(3)#2	104.0(3)
Be(1)−O(2)#1	1.632(6)	O(1)−Be(1)−O(2)#1	113.7(3)
O(4)−P(1)−O(2)	113.0(2)	O(4)#4−Be(1)−O(2)#1	111.1(3)
O(4)−P(1)−O(1)	105.7(2)	O(3)#2−Be(1)−O(2)#1	104.3(3)
O(2)−P(1)−O(1)	112.3(2)		

[a] Symmetry transformations used to generate equivalent atoms for $BePO_4$−GME1: #1, $y, x, z - {}^1/_2$; #2, $y, -x + y, -z$; #3, $-x + 1, -y + 1, -z$; #4, $y, x, z + {}^1/_2$; #5, $x-y, x, -z$; #6, $x, x-y + 1, -z + {}^1/_2$; #7, $-y + 1, x - y + 1, z$; #8, $-x + y, -x + 1, z$; #9, $-x + y, y, -z + {}^1/_2$; #10, $-y + 1, -x + 1, -z + {}^1/_2$; #11, $y, -x + y + 1, -z$; #12, $x - y, -y + 1, z + {}^1/_2$; #13, $-x + 1, -x + y + 1, z + {}^1/_2$; #14, $-y + 1, -x + 1, -z - {}^1/_2$; #15, $-x + y + 2, -x + 1, z$; #16, $-x + y + 2, y, -z + {}^1/_2$; #17, $x, x - y - 1, -z + {}^1/_2$; #18, $-y + 1, x - y - 1, z$. [b] Symmetry transformations used to generate equivalent atoms for $BePO_4$−GIS: #1, $x - {}^1/_2, -y + {}^1/_2, z$; #2, $-x + 1, -y, z - {}^1/_2$; #3, $-x + 1, -y, z + {}^1/_2$; #4, $x + {}^1/_2, -y + {}^1/_2, z$. [c] Symmetry transformations used to generate equivalent atoms for $BePO_4$−ABW: #1, $-x + 1, y, -z + {}^1/_2$; #2, $-x + {}^1/_2, -y + {}^3/_2, -z$; #3, $x, -y + 1, z + {}^1/_2$; #4, $x, -y + 1, z - {}^1/_2$; #5, $-x + 1, y, -z + {}^3/_2$; #6, $-x + {}^3/_2, -y + {}^3/_2, -z + 2$; #7, $-x + 1, -y + 2, -z + 2$.

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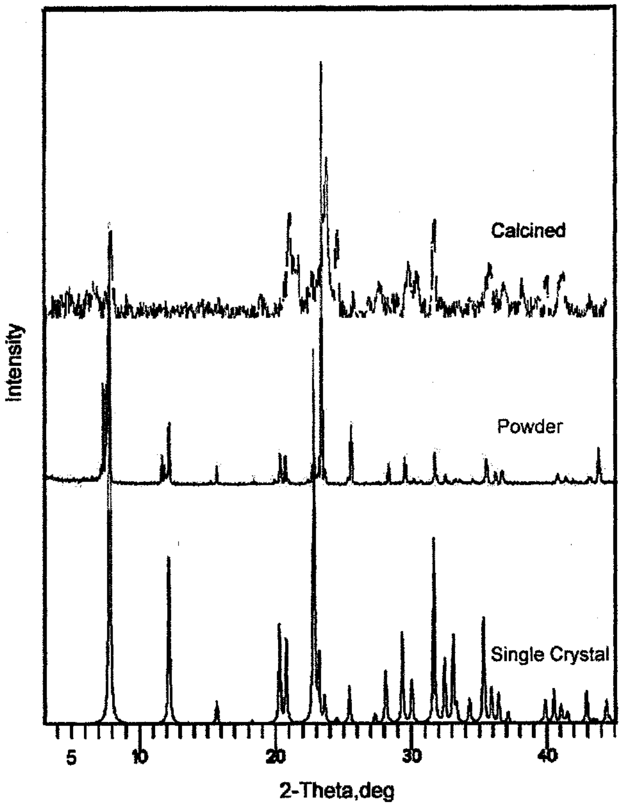

Figure 1. X-ray powder diffraction pattern, single-crystal pattern, and calcined (400 °C in air) $BePO_4$−GME sampler.

phase GME-type beryllophosphate for the first time. When polyethylene polyamine $[C_{2n}H_{3+5n}N_{1+n}$ $(n \geq 5)]$ is used as a structure-directing agent (SDA), pure $BePO_4$−GME crystal (ca. 50 × 100 × 150 μm) with a different morphology (rectangular polyhedron) can also be prepared (Figure 2d). $BePO_4$−GME can be prepared in a relatively broad range of pH values (from 6.6 to 10.4) by a change in the Be/P ratio and amine/Be, but only concentrated amine can result in the pure phase. The dimension of a crystal can be controlled by adding, to a small amount of sodium, potassium and NH_4^+ (Table 1), When concentrated piperazine is used as the template, another pure phase beryllophosphate structure ($BePO_4$−GIS) with cubic polyhedron morphology (ca. 150 × 100 × 50 μm) (Figure 2e) is obtained. The crystallization of $BePO_4$−GIS is very sensitive to the pH value of the gel solution; only concentrated piperazine can give pure $BePO_4$−GIS phase. A large cubelike single crystal (ca. 150 × 50 × 50 μm) (Figure 2f) of beryllophosphate zeolite analogue with pure ABW topology structure (denoted as $BePO_4$−ABW) can be formed by using a concentrated pyridine as the template.

Structure of $BePO_4$−GME. As shown in Figure 3, $BePO_4$−GME consists of a three-dimensional anionic Be/P/O framework that encloses a one-dimensional 12-membered ring channel, which is occupied by protonated triethylene tetramine molecules. $BePO_4$−GME has the same topology as the known zeolite gmelinite framework, which is based on the network of strictly alternating BeO_4 and PO_4 tetrahedral in which all vertexes are shared. The elemental analysis results based on inductively coupled plasma (ICP) show the Be/P atomic ratio of $BePO_4$−GME is 1.0. Figure 4 shows the structure is built from the stacking of 6-membered rings with the AABB sequence, which forms a $[8^{3}6^{4}4^{24}]$ cage. Different sequences of 6-membered rings cause different topologies, for example, chabazite (CHA) (AABBCC) and AFT (AABBCCAACCBB). We have also successfully synthesized a $CoPO_4$−CHA with the AABBCC sequence of the 6-membered rings. The $[8^{3}6^{4}4^{24}]$ cage is only found in the AFT topology because of the existence of a CCAACC or BBAABB fragment sequence. The characteristic topological features of the $BePO_4$−GME structure include the double 6-membered rings and 4.8.8 net, which has been found in a variety of structures (ABW, GIS, DFT,[7] and PHI[9]). In $BePO_4$−GME the 4.8.8 nets are stacked along the c-axis, creating a 12-membered ring channel in the crystallographic [001] direction. The beryllium atoms form Be−O−P bonds to four distinct phosphorus atom neighbors with the average distance of $d_{av}(Be-O) = 1.621$ Å (Table 4). The mineral gmelinite $(Na_2,Ca)_4[Al_8Si_{16}O_{48}]\cdot 24H_2O$ is hexagonal ($P6_3/mmc$) and the cell parameters are $a = 13.8$, $c = 10.0$ Å, and $V = 1594.5$ Å^3; the crystallographic symmetry of $BePO_4$−GME is trigonal ($P\bar{3}1c$), which is a subgroup of $P6_3/mmc$ ($a = 13.05$, $c = 9.48$ Å, and $V = 1400$ Å^3). The framework contraction is caused by beryllium and phosphorus atoms occupying the tetrahedron site. The negative charges of $BePO_4$−GME $(C_6H_{21}N_4)Na_3Be_6P_6O_{24}\cdot 3H_2O$ are balanced by the protonated triethylene tetramine and sodium cation. The framework tetrahedral atom density (the number of T-atoms in 1000 Å^3) for $BePO_4$−GME is 17.1.

After calcination at 400 °C in air, the diffraction peaks become weaker and shift to a little higher angle (Figure 1) because of lattice contraction and segmental framework collapse. TGA/DTA analysis of $BePO_4$−GME shows that an extraframework species is present. For $BePO_4$−GME, up to 1000 °C, there was only one single-step weight loss of 30% between 310 and 470 °C, accompanied by a large exothermic peak. The total weight loss corresponds to the removal of the organic molecule and H_2O from the structure (experimental, 30%; theoretical, 31.5%). In addition, there was a series of small exothermic peaks between 630 and 730 °C. It was possibly caused by the collapse of the framework.

Structure of $BePO_4$−GIS. The structure of $BePO_4$−GIS prepared from pyridine is also based on a network of strictly alternating BeO_4 and PO_4 tetrahedral in which all the vertexes are shared (Figure 5). The framework structure consists of three types of channels with windows containing eight T-atoms (T = Be and P). The two same elliptical channels with dimensions of 5.7 × 7.8 Å are along the [001] and [010] direction and the third channel is along the [111] direction (Figure 6). The basic building unit (BBU) of $BePO_4$−GIS can be considered a saddleback polyhedron that consists of three edge-sharing 4-membered rings (Figure 7a). Two such units can be connected in two ways to create new four-membered rings and 8-membered rings in $BePO_4$−GIS.One type of connection by dip−dip T-atoms can form the 4-membered rings and another type of connection by peak−peak T-atoms can form the 8-membered rings. Thus, these two types of connections generate a 4.8.8 network (Figure 7b), which also can be

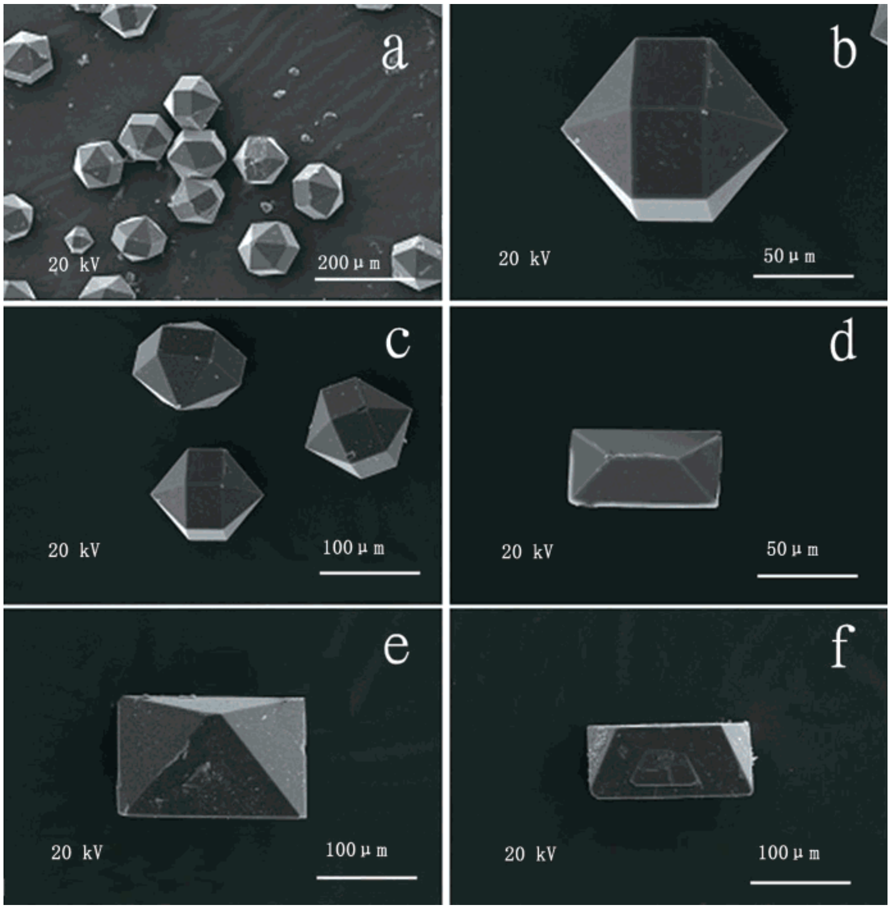

Figure 2. SEM images showing morphologies and sizes of as-synthesized beryllophosphate compounds: (a) the pure phase of the as-synthesized $BePO_4$−GME prepared with concentrated triethylene tetramine; (b) the hexagonal gyroid morphology of $BePO_4$−GME; (c) the single crystal (ca. 150 × 150 × 150 μm) of $BePO_4$−GME; (d) as-synthesized $BePO_4$−GME prepared with polyethylene polyamine; (e) as-synthesized $BePO_4$−GIS prepared with piperazine; (f) as-synthesized beryllophosphate molecular sieve with ABW topology prepared by using pyridine as the structure-directing agent.

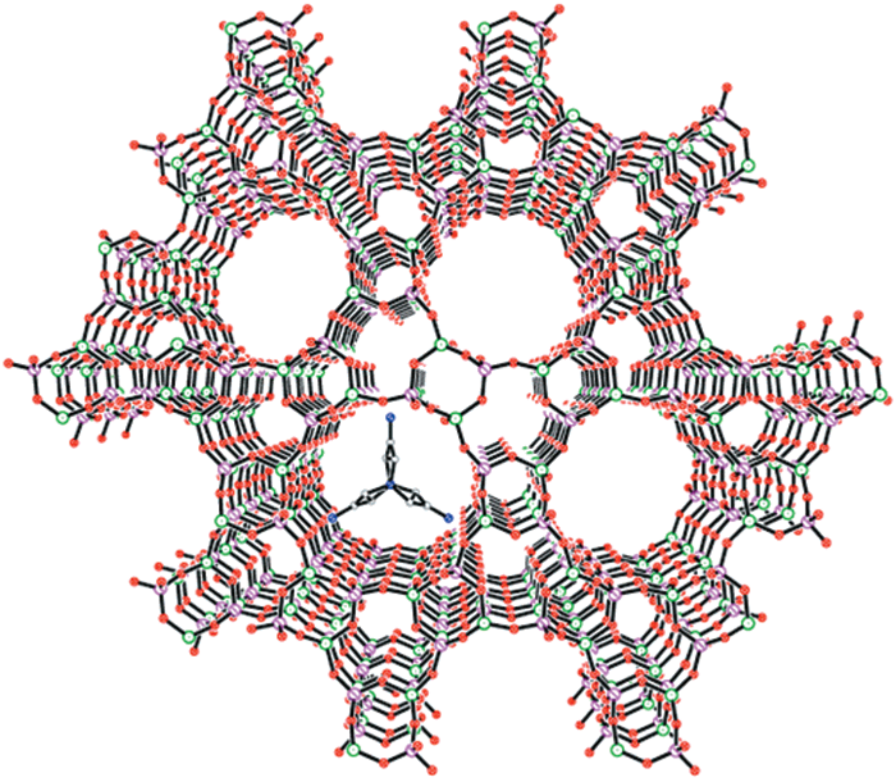

Figure 3. Framework of beryllophosphate $BePO_4$−GME viewed along the *c*-axis, showing the channels enclosed by 12-membered tetrahedral rings.

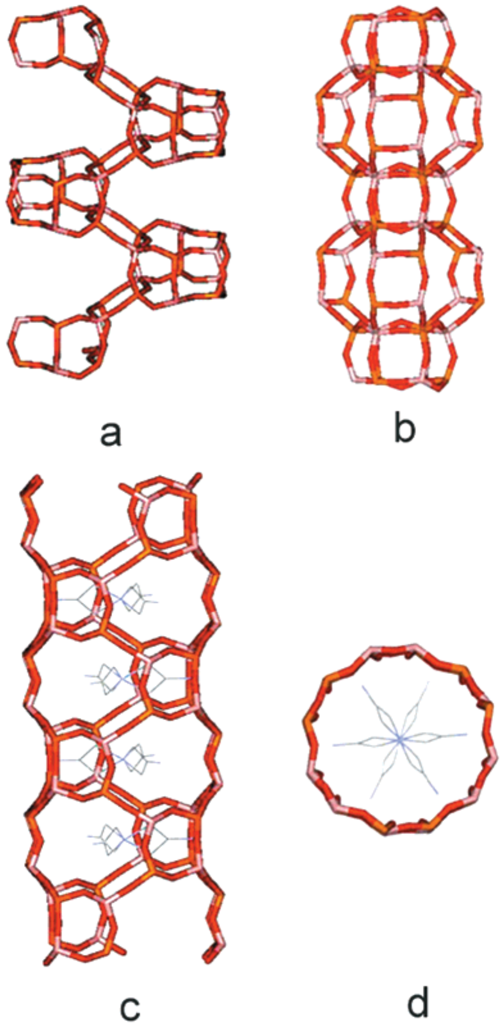

Figure 4. Subunits of $BePO_4$−GME: (a) the AABB sequence of double 6-membered rings, (b) the $[8^36^44^{24}]$ cage of $BePO_4$−GME, (c) the 4.8.8 net for $BePO_4$−GME along the *c*-axis, and (d) the 12-membered ring channel occupied by triethylene tetramine molecule, C2 atoms has two orientations.

found in the $BePO_4$−GIS framework. The 4.6 net and the 4.6.8 net that have been found in many zeolite topologies can also be created by different types of connections between those BBUs (such as DFT). The charges of framework are balanced by the protonated amine and the framework density (FD) is 19.0 per 1000 Å^3. $BePO_4$−GIS has quite a distorted framework and space group (*C*2/*c*) with the unit cell axes different from conventional GIS cell axes, which are based on more orthorhombic cells (90° × 90° × 90°), so $BePO_4$−GIS is an isostructure to ACP-GIS1.[5]

Structure of $BePO_4$−ABW. A dozen structures with ABW-type topology already tabulated before. In our work, a pure $BePO_4$−ABW phase can be prepared by using pyridine as both the solvent and template. The $BePO_4$−ABW structure is built from the stacking of 4.8.8 nets, it is orthorhombic (space group: $Pna2_1$), and the space group is typical of zeolite ABW structures.[14] The hydrolysis of the initial amine produced the NH_4^+ cation to balance the charge of the framework. The framework density for $BePO_4$−ABW is 21.5/1000 Å^3.

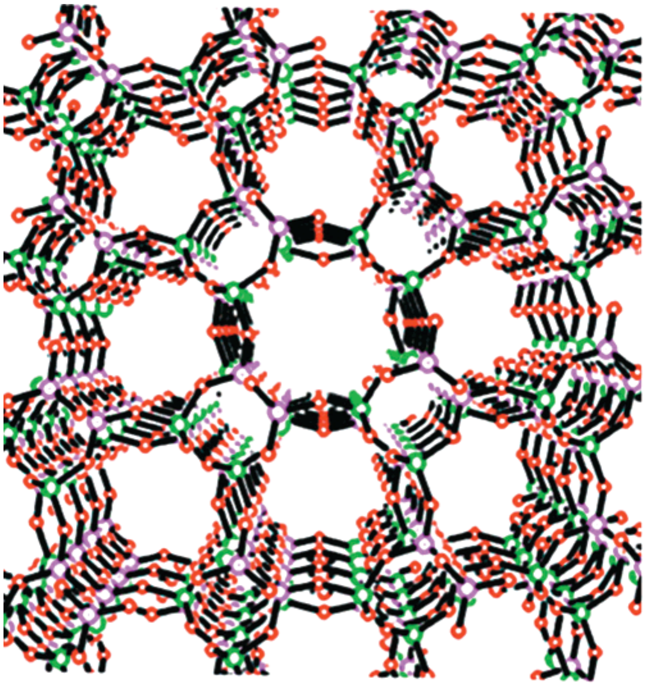

Figure 5. The 4.8.8 network of strictly alternating BeO_4 and PO_4 tetrahedral in which all the vertexes have a shared viewed down the *c*-axis in $BePO_4$−GIS.

Interestingly, the three pure beryllophosphates synthesized with the concentrated amine templating have similar structural characterization. They all have a 4.8.8 network in their frameworks and can be viewed as being built from a different number of cross-linked chains (threes for $BePO_4$−GME and fours for $BePO_4$−GIS and $BePO_4$−ABW). It suggests the frameworks of beryllophosphates have the tendency to form 4- and 8-membered rings in concentrated amines conditions.

Templating Effect of Guest Species. The location of the overall amine molecules in $BePO_4$−GME can be defined except the H atoms for C2 because some disordered orientations for C1 atoms are also observed (Figure 8). Triethylene tetramine molecules have two orientations that occupy the center of the 12-membered ring channel within the structure. An important symmetry element of triethylene tetramine is the 3-fold axis. When triethylene tetramine is used as the SDA, the same symmetry element (3-fold axis) is observed in the resulting structure. The axis is aligned along the 12-membered ring channel direction in the $BePO_4$−GME structure. Triethylene tetramine can be regarded as a true template for the formation of the structure. The amine molecules alternated by a 60° angle along the *c*-axis direction form a cylindrical with a diameter of ∼6.1 Å, which would fit comfortably with the 10-Å dimensions of the channels (see Figure 4c,d). The strong hydrogen bonding between all end nitrogen atoms and the corresponding framework oxygen atoms is observed (the shortest N−O's have a distance of 2.93 Å); it makes the framework assembly according to the shape and size of the amine molecule. The amine can be partially removed (about 80%) after calcination at 400 °C. Trying to remove all amines from $BePO_4$−GME is unsuccessful. When small amine molecules such as piperazine and

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[14] Bu, X.; Feng, P.; Gier, T. E.; Stucky, G. D. *Zeolites* **1997**, *19*, 200.

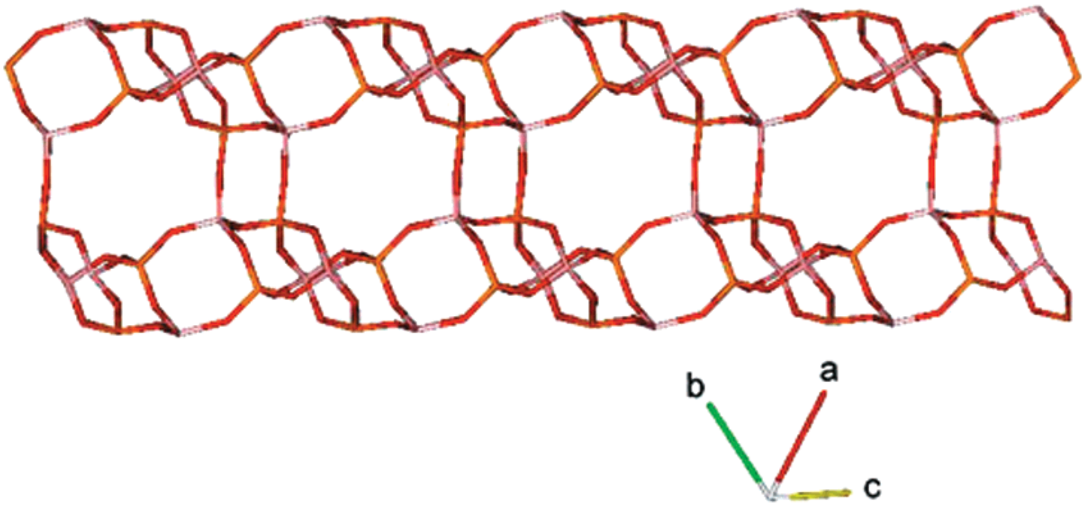

Figure 6. The 8-membered rings channel along the crystallographic [111] direction in $BePO_4$−GIS.

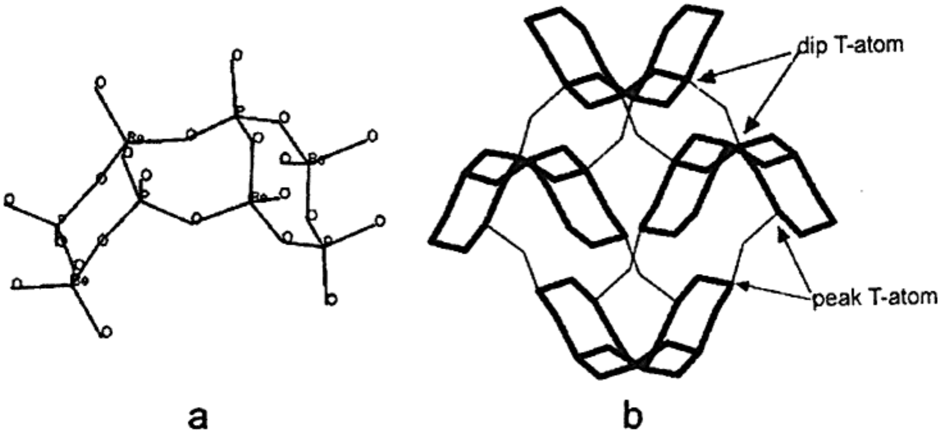

Figure 7. The basic building unit consists of $BePO_4$−GIS: (a) BBU consists of three edge-sharing 4-membered rings; (b) the connection of four BBUs created new 4- and 8-membered rings.

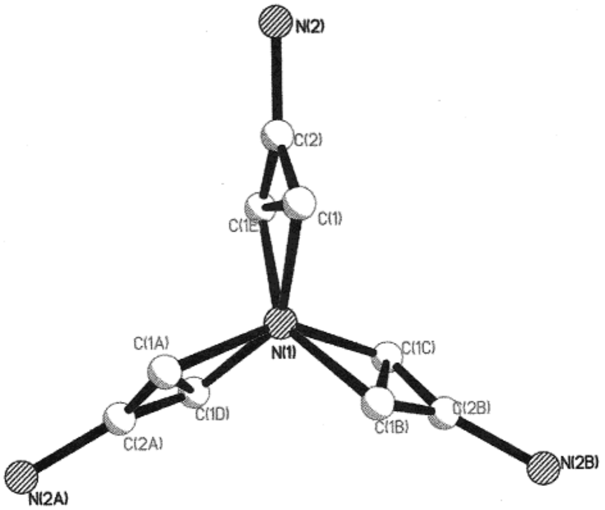

Figure 8. Two possible orientations of triethylene tetramine molecules in $BePO_4$−GME.

pyridine are used as the templates, 8-membered ring small channel structures of GIS and ABW are formed.

Conclusions

In summary, a few pure beryllophosphate molecular sieves with a topology similar to those of the gmelinite, gismondine, and ABW frameworks have been hydrothermally synthesized with concentrated amines such as triethylene tetramine, piperazine, and pyridine as structure-directing agents.

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Supporting Information Available: CIF data, anisotropic displacement parameters ($A^2 \times 10^3$) for $BePO_4$−GME, $BePO_4$−GIS, and BePO4−ABW, and ORTEP drawings showing the local coordination environment of $BePO_4$−GME and $BePO_4$−GIS (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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