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Hydrothermal synthesis and low temperature crystal structure of an ammonium beryllophosphate with the merlinoite topology

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Abstract

An ammonium beryllophosphate (BeP-MER1) with the merlinoite framework topology has been made by the hydrothermal synthesis. Similar to the mineral merlinoite, BeP-MER1 belongs to the orthorhombic space group, but its unit cell is metrically tetragonal. The framework of a merlinoite structure such as BeP-MER1 can be viewed as the body-centered tetragonal packing of double 8-rings or the stacking of 4.8.8 nets along the *c*-axis. BeP-MER1 has three-dimensional, intersecting 8-ring channels along the crystallographic [001], [110] and [1$\bar{1}$0] directions. The sites of extra-framework species are located, but the distribution of H_2O and NH_4^+ among these sites are not unambiguously determined. A summary of beryllophosphate zeolite structures provides an interesting comparison among hydrous and anhydrous alkali metal templated beryllophosphate phases.

Keywords: Beryllophosphate; Beryllium phosphate; Crystal structure; Merlinoite; Zeolite analog; Zeolite structure

1. Introduction

Zeolites are three-dimensional aluminosilicates with open-framework structures and some of them such as zeolites A, X, and Y have important industrial applications [1]. Since 1950s, there have been extensive studies aimed at the synthesis of new zeolite type materials with the expectation that these materials can lead to new and improved industrial processes [2]. A breakthrough occurred in early 1980s with the synthesis of a large family of aluminophosphate based zeolite type materials [3]. Since then, the chemical compositions of zeolite type materials have been greatly expanded to include a variety of chemical elements capable of tetrahedral coordination [4]. In addition, there have been much interests in microporous materials containing non-tetrahedral metal atoms. For example, an impressive success has been achieved in the synthesis of microporous materials containing V and Mn [5,6].

We have been interested in zeolite type structures based on divalent and pentavalent tetrahedral atoms (T^{2+} such as Be^{2+}, Zn^{2+}, Co^{2+} and T^{5+} such as P^{5+}, As^{5+}) for some time and have synthesized over a hundred new T^{2+}/T^{5+} based oxide materials, many of which are zeolite analogs [7–9]. However, despite the impressive successes in the synthesis of phosphate based zeolite type materials, some zeolite structures are still only found

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as silicates [10]. Thus, one of the challenges facing a synthetic chemist is the synthesis of all aluminosilicate zeolites (except those with 5-rings such as ZSM-5, -11) in the phosphate system.

The divalent-metal–rich phosphates have a variety of zeolite type structures, encompassing nearly all typical zeolite structural features (5-rings being one exception) such as double 4-rings (ACP-1), double 6-rings (ACP-CHA series and UCSB-6, -10 series) and double 8-rings (ACP-MER series and UCSB-8 series), α-cages (CAP-RHO1, MAP-RHO1, and MnAP-RHO1), β-cages (ACP-SOD series), γ-cages (ACP-MER series) and ϵ-cages (UCSB-6, -10 series) [11,12]. While fibrous zeolites have been traditionally difficult to synthesize as phosphates, about a dozen thomsonite and edingtonite analogs have already been made [12,13]. Such a structural diversity demonstrates the great potential of the divalent-metal-rich phosphate system.

From a structural point of view, beryllium is ideally suited as building blocks for new zeolite structures because it is always tetrahedrally coordinated to oxygen atoms and its size (0.27 Å) is similar to other commonly used tetrahedral atoms such as Si^{4+} (0.26 Å) and P^{5+} (0.17 Å). Beryllium also has a tendency to form 3-membered rings, which have been reported to be useful for the construction of very low framework density structures [14]. A number of Be-containing zeolite structures are known. To the best of our knowledge, beryllium is the only divalent metal that has been found in the framework of zeolite minerals. In addition to several minerals (chivavennite, lovdarite, roggianite and weinebeneite) and one synthetic compound (beryllophosphate-H), which possess unique structure types, some Be-containing zeolite analogs are also known in a number of zeolite structure types including ABW, ANA, CAN, EDI, FAU, GIS, LOS, RHO and SOD (Table 1).

In this paper, we report a hydrated beryllophosphate isotypic to the mineral merlinoite, a rare zeolite mineral with double 8-rings. It should be noted that before the synthesis of amine-templated cobalt phosphate based zeolite merlinoite analogs (ACP-MER1, ACP-MER2, ACP-MER3, and ACP-MER4) very recently, [12,15] the merlinoite framework topology was only known in silicates.

Table 1
A summary of beryllophosphate zeolite structures prepared through direct synthesis

Cation	Chemical composition	Structure type
Li^+	$Li_4Be_4P_4O_{16}\cdot 4H_2O$ [7]	ABW
Li^+	$Li_{24}Be_{24}P_{24}O_{96}\cdot 40H_2O$ [19]	RHO
Li^+	$Li_8Cl_2Be_6P_6O_{24}$ [20]	SOD
Li^+	$Li_8Br_2Be_6P_6O_{24}$ [21]	SOD
Li^+	$Li_8(HPO_4)(BePO_4)_6\cdot H_2O$ [22]	LOS
Na^+	$Na_8Be_8P_8O_{32}\cdot 10H_2O$ [19]	GIS
Na^+	$Na_{96}Be_{96}P_{96}O_{192}\cdot 192H_2O$ [7]	FAU
Na^+/K^+	$(Na_7K_7)Be_{14}P_{14}O_{56}\cdot 20H_2O$ [19]	BPH
K^+	$K_{10}Be_{10}P_{10}O_{40}\cdot 10H_2O$ [19]	EDI
K^+	$KBePO_4$ [19]	ABW
Rb^+	$RbBePO_4$ [23]	ABW
Cs^+/H^+	$(Cs_{16}H_8)Be_{24}P_{24}O_{96}$ [19]	ANA
Cs^+	$CsBePO_4$ [23]	ABW
NH_4^+	NH_4BePO_4 [24]	ABW
NH_4^+	$NH_4BePO_4\cdot 1/8H_2O$	MER

2. Experimental

2.1. Synthesis

Warning! Beryllium compounds are extremely toxic, observe all appropriate safety precautions in handling these phases, particularly Be oxide dusts and Be solutions. 6.60 g 2 M H_3PO_4 (12 mmol), 2.59 g *t*-octylamine (20 mol), 2.91 g 2 M $Be(NO_3)_2$ (5 mmol) and 10 ml H_2O were sealed in a teflon pouch and heated under autogenous (80 psi water) pressure in an autoclave at 150°C for 7 days. Standard filtration and recovery techniques yielded 0.59 g of a mixture of white powder and small transparent crystals. Separation was achieved by ultrasonic decantation to give materials suitable for the structure determination. Two different phases were recognized based on the crystal morphology. The needle shaped crystals were a minor phase and were identified as NH_4BePO_4 with the ABW structure, while cube-like crystals $NH_4BePO_4\cdot 1/8H_2O$ were reported here.

2.2. Single crystal analysis

A crystal was glued to a thin glass fiber with epoxy resin and mounted on a Siemens SMART CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (MoKα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. An Oxford cryostream provides a temperature range from 80 to 375 K with a stability of about 0.1 K. About 1.3 hemisphere of intensity data were collected in 1321 frames with ω scans (width of 0.30° and exposure time of 30 s per frame) at both room temperature and at 150 K. The empirical absorption corrections were based on the equivalent reflections and other possible effects such as absorption by the glass fibre were simultaneously corrected. The structure was solved by direct methods followed by successive difference Fourier methods. All calculations were performed using SHELXTL running on Silicon Graphics Indy 5000. Final full-matrix refinements were against F^2. Since the difference between the room temperature data and low temperature data is insignificant, only low temperature results are reported here. The crystallographic data are summarized in Table 2. Positional coordinates are listed in Table 3 while selected bond distances and angles are given in Table 4.

Table 2
A summary of crystal data and refinement results

Name	BeP-MER1
Formula	$NH_4BePO_4 \cdot 1/8H_2O$
Habit	Cube
Color	Clear
Size (μm)	$80 \times 80 \times 80$
Temp (K)	150
a (Å)	18.0209(1)
b (Å)	17.9564(4)
c (Å)	9.4623(2)
V (Å^3)	3061.9(1)
Z	32
Space group	*Ccca*
$2\theta_{max}$ (°)	56
Total data	8843
Unique data	1852
Data with $I > \sigma 2(I)$	1362
Parameters	167
$R(F)$ (%) [a]	4.72
R_w (F^2) (%)	9.59
GOF	1.02

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with $F_o > 4.0\ \sigma(F)$.

3. Results and discussions

One interesting structural feature of merlinoite structures is the pseudo-tetragonal cell. Even though the unit cell of BeP-MER1 is metrically tetragonal [at room temperature, $a = 18.0156(6)$, $b = 18.0190(6)$, $c = 9.4787(3)$], the true crystallographic symmetry of BeP-MER1 is orthorhombic. There is no ambiguity in determining the lattice symmetry because the intensity data clearly violates the tetragonal symmetry. The merging R factor is as high as 41% in the tetragonal system, as compared to only 6.6% in the orthorhombic system. Note that such a pseudo-symmetry is not uncommon in merlinoite structures. The mineral merlinoite [$K_5Ca_2(AL_9Si_{23}O_{64}) \cdot 24H_2O$] is also orthorhombic (*Immm*), but has a tetragonal cell ($a = 14.1$ Å, $b = 14.2$ Å, $c = 10.0$ Å) [10]. On the other hand, the unit cell of a merlinoite type structure is not always metrically tetragonal. For example, in ACP-MER1, the a length differs significantly from the b length [12]. The true tetragonal symmetry is, however, also possible and has been found in three amine-templated aluminum cobalt phosphate analogs (ACP-MER2, ACP-MER3 and ACP-MER4) [12,15].

The characteristic topological features of merlinoite structures include the double 8-rings (Fig. 1) and 4.8.8 nets. No other zeolite structures have the combination of these two structural features [10]. In addition to merlinoite structures, double 8-rings are only known in rho, paulingite and UCSB-8 [10,11]. The 4.8.8 nets are, however, significantly more common and have been found in a variety of structures including ABW, gismondine, phillipsite, ACP-1, and UCSB-3 [16,17]. In BeP-MER1, the 4.8.8 nets are stacked along the c-axis, creating 8-ring channels in such a direction. Other 8-ring channels are along the crystallographic [110] and [1$\bar{1}$0] directions. Thus, BeP-MER1 has three-dimensional intersecting, orthogonal 8-ring channels.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$). $\boldsymbol{U}$(eq) is defined as one third of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor

	x	y	z	$\boldsymbol{U}$(eq)
P(1)	1734(1)	3121(1)	700(1)	9(1)
P(2)	926(1)	4587(1)	3689(1)	10(1)
Be(1)	2902(2)	3413(2)	−1355(4)	12(1)
Be(2)	607(2)	4250(2)	780(4)	12(1)
O(1)	2068(1)	3429(1)	−677(2)	15(1)
O(2)	913(1)	4731(1)	2091(2)	14(1)
O(3)	928(1)	3409(1)	787(2)	14(1)
O(4)	272(1)	4119(1)	4193(2)	16(1)
O(5)	1660(1)	2276(1)	678(2)	15(1)
O(6)	914(1)	5364(1)	4373(2)	16(1)
O(7)	1654(1)	4189(1)	4106(2)	14(1)
O(8)	2198(1)	3400(1)	1948(2)	15(1)
O(9)	0	2500	2500	31(1)
N(1)	0	2500	−984(4)	13(1)
N(2)	2500	5000	1070(5)	18(1)
N(3)	1098(2)	6413(2)	1945(4)	23(1)
H(11)	−286(20)	2220(20)	−436(37)	42(13)
H(12)	150(52)	2067(25)	−1347(78)	164(35)
H(21)	2188(27)	5289(28)	521(54)	62(16)
H(22)	2753(20)	5329(21)	1626(41)	25(10)
H(31)	755(25)	6705(24)	1866(46)	30(12)
H(32)	945(32)	5853(38)	1919(68)	97(21)
H(33)	1483(37)	6526(34)	2614(79)	101(22)
H(34)	1303(44)	6500(41)	1177(89)	120(29)
H(9)	373(30)	2161(32)	3119(64)	0(14)

Merlinoite structures can be simply viewed as body-centered tetragonal packing of double 8-rings (Fig. 1). The body-centered packing of double 4-rings has been found in a newly discovered aluminum cobalt phosphate structure, ACP-1 [12]. Some other zeolites such as UCSB-8 can also be viewed as body-centered packing of polyhedral units that are much larger than double 8-ring units [11]. Another way to view the merlinoite framework is based on the cross-linked chains. The chains consist of alternating double 8-rings and γ-cages [1] and propagate along the c-axis (Fig. 2). Two adjacent chains are displaced by half of the c-axis.

It is of interest to note that the synthesis product also contains a small amount of NH_4BePO_4, a zeolite ABW analog (Table 1). Since both ABW and MER structures are built from the stacking of 4.8.8 nets, it is tempting to suggest that the merlinoite structure ($NH_4BePO_4 \cdot 1/8H_2O$) may undergo a phase transformation into the ABW structure upon the loss of the lattice water. It has been proposed before that ABW structures are thermodymically stable phases for large extra-framework cations such as Rb^+ and Cs^+ in the $ABCO_4$ family of structures (A, B, C refer to cations) [18].

Table 4
Selected bond lengths (Å) and angles (°)

P(1)–O(5)	1.523(2)	P(1)–O(8)	1.530(2)
P(1)–O(1)	1.539(2)	P(1)–O(3)	1.544(2)
P(2)–O(4)	1.523(2)	P(2)–O(2)	1.534(2)
P(2)–O(6)	1.537(2)	P(2)–O(7)	1.547(2)
Be(1)–O(5)	1.602(4)	Be(1)–O(8)	1.616(4)
Be(1)–O(1)	1.633(4)	Be(1)–O(7)	1.664(4)
Be(2)–O(6)	1.600(5)	Be(2)–O(4)	1.602(4)
Be(2)–O(2)	1.609(4)	Be(2)–O(3)	1.617(4)
O(5)–Be(1)–O(8)	116.1(3)	O(5)–Be(1)–O(1)	108.1(3)
O(8)–Be(1)–O(1)	106.8(2)	O(5)–Be(1)–O(7)	107.7(3)
O(8)–Be(1)–O(7)	109.0(2)	O(1)–Be(1)–O(7)	109.0(2)
O(6)–Be(2)–O(4)	114.7(3)	O(6)–Be(2)–O(2)	106.9(3)
O(4)–Be(2)–O(2)	113.9(3)	O(6)–Be(2)–O(3)	106.5(3)
O(4)–Be(2)–O(3)	102.5(2)	O(2)–Be(2)–O(3)	112.0(3)
P(1)–O(1)–Be(1)	133.3(2)	P(2)–O(2)–Be(2)	132.5(2)
P(1)–O(3)–Be(2)	130.5(2)	P(2)–O(4)–Be(2)	133.5(2)
P(1)–O(5)–Be(1)	136.1(2)	P(2)–O(6)–Be(2)	138.4(2)
P(2)–O(7)–Be(1)	136.8(2)	P(1)–O(8)–Be(1)	135.3(2)

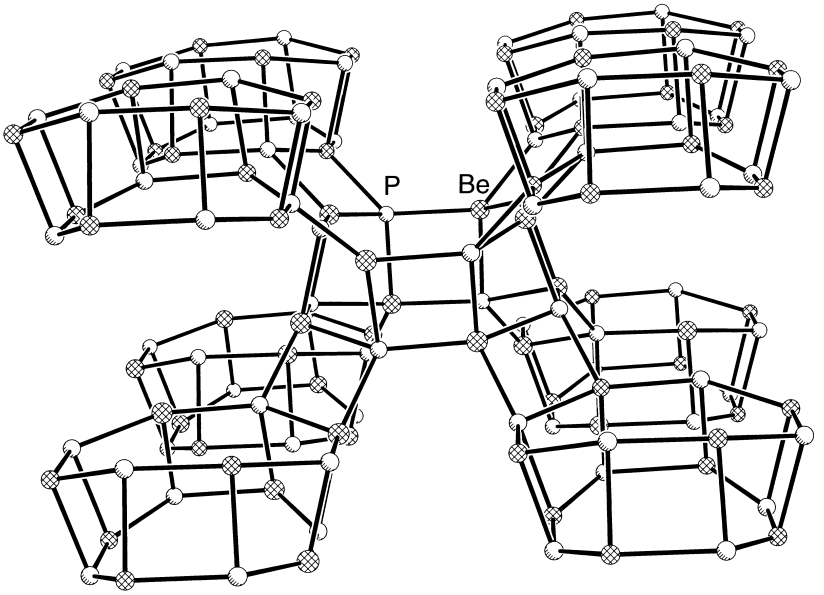

Fig. 1. The body-centered packing of double 8-rings in BeP-MER1. Oxygen atoms are not shown.

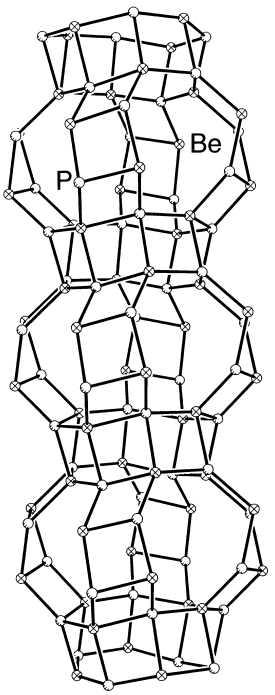

Fig. 2. The γ-cages are connected through double 8-rings to form a chain along the crystallographic c-axis in BeP-MER1. Oxygen atoms are not shown.

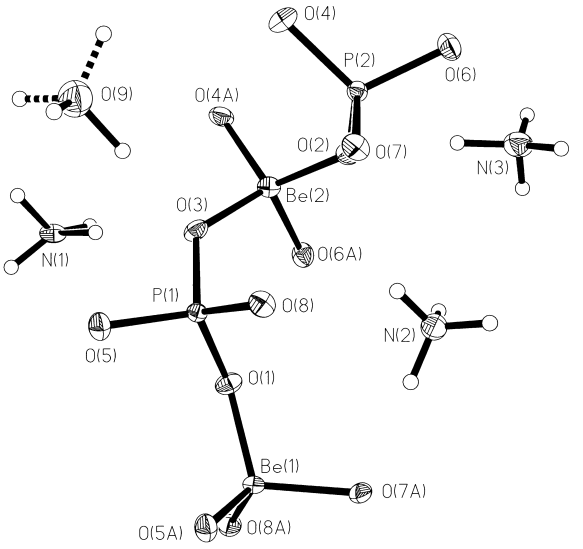

Fig. 3. The ORTEP drawing (50%) showing the local coordination environment. Atoms with labels containing 'A' are generated by symmetry. Two possible orientations of water molecules are shown.

There are four distinct extra-framework sites, occupied by either H_2O or NH_4^+ (Fig. 3). Due to the difference in multiplicity of these sites, there is

only one possible way to assign H_2O and NH_4^+ to these sites (one site for H_2O, and three sites for NH_4^+) so that the charge neutrality can be maintained. However, hydrogen atomic positions can be experimentally determined in this case and the large variation in the magnitude of thermal parameters of these hydrogen atoms indicate that there is a partial exchange between H_2O and NH_4^+ positions. For example, the thermal parameter of the hydrogen atom (H9) located on the water molecule is very small. This can be explained by the partial occupancy of the water site with NH_4^+ cations, which leads to the increased electron density at hydrogen atom sites surrounding the water molecule (Fig. 3).

The presence of N–H…O or O–H…O type hydrogen bonds with framework oxygen atoms is suggested by the short N…O (or O…O) distances. The shortest contact distances are 2.845, 2.876, 2.811 and 2.863 Å for O9–O3 (O9 represents the water molecule), N1–O3, N2–O7 and N3–O1, respectively. The short distance of 2.925 Å from N1 to N3 sites suggests the presence of hydrogen bonds between extra-framework species.

In conclusion, a zeolite merlinoite analog has been prepared for the first time in a binary phosphate system, further demonstrating the rich synthetic and structural chemistry of the beryllophosphate system.

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