ELSEVIER

Structural and chemical studies of zeolite ABW type phases: Syntheses and characterizations of an ammonium zincophosphate and an ammonium beryllophosphate zeolite ABW structure

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Hydrothermal syntheses and X-ray crystal structures of two framework phosphates are described. The framework topologies of NH_4ZnPO_4 and NH_4BePO_4 are the same as that of the zeolite ABW type. Preparation of these two compounds is a rare example of the direct synthesis of ammonium zeolite analog structures. The framework can be considered as built from the stacking of hexagonal layers. A literature study of $ABCX_4$-type structures reveals more than two dozen compounds with the ABW-type topology in addition to about a dozen structures already tabulated. The newly discovered materials with the ABW topology have diverse chemical compositions and display various lattice symmetries. Other interesting properties of these ABW phases include displacive phase transitions and crystal twinning. The compositional and structural diversities of these ABW phases have important implications for the future design of new zeolite phases. Crystal data for NH_4ZnPO_4: M = 178.38, space group $P2_1$(No. 4), a = 8.7966(5)Å, b = 5.4565(3)Å, c = 8.9654(5)Å, β = 90.323(1)°, V = 430.75(1)Å^3, Z = 4, D_c = 2.753 g cm^{-3}, Mo$K\alpha$, μ = 5.970 mm^{-1}, $2\theta_{max}$ = 56.00°, R(F) = 3.88% for 129 parameters and 1769 reflections with $I > 2\sigma(I)$. Crystal data for NH_4BePO_4: M = 122.02, space group $Pna2_1$ (No. 33), a = 8.7196(7)Å, b = 8.5919(7)Å, c = 4.9661(4)Å, V = 372.05(5)Å^3, Z = 4, D_c = 2.178 g cm^{-3}, Mo$K\alpha$, μ = 0.608 mm^{-1}, $2\theta_{max}$ = 56.46°, R(F) = 2.77% for 81 parameters and 840 reflections with $I > 2\sigma(I)$.

Keywords: Zincophosphate; beryllophosphate; zeolite ABW; zeolite analogs

INTRODUCTION

Microporous aluminosilicates are produced in ton quantities annually for a variety of commercially important uses.[1] Since the 1980s, there has been an intense search for materials with new framework topologies or compositions with the expectation that such materials could lead to new applications.[2] As a result, many novel framework structures based on aluminophosphates,[3] gallophosphates,[4] and vanadium phosphates,[5,6] etc., have been synthesized and characterized. Recently, a number of open-framework zinco (or beryllo) phosphates (or arsenates) have been reported, some of which have the same framework topologies as zeolitic aluminosilicates.[7] These include $Na_6(H_2O)_8(ZnPO_4)_6$(sodalite), $(Na,TMA)_{96}M_{96}P_{96}O_{192}$ (M = Be or Zn, zeolite X), $Li_4M_4P_4O_{16} \cdot 4H_2O$ (M = Be or Zn, zeolite Li-ABW), and $Li_{24}Be_{24}P_{24}O_{96} \cdot 40H_2O$ (zeolite RHO),[8] most of which were synthesized at low temperatures (100°C or below) and were characterized with X-ray powder methods since only polycrystalline products were obtained.[7]

Here, we report two new divalent metal phosphates with the zeolite ABW topology: NH_4ZnPO_4 and NH_4BePO_4. The negative framework charge of these two compounds is balanced by extra-framework NH_4^+ cations. Preparation of these two salts is a rare example of the direct synthesis of an ammonium zeolite analog structure. Together with NH_4CoPO_4 reported previously,[9] they are the only known ammonium ABW salts. Extra-framework ammonium cations in microporous aluminosilicates are usually introduced through ion-exchanges as in the cases of ammonium zeolite A,[10] zeolite Q,[11] and faujasite.[12]

The zeolite ABW-type topology is adopted by a variety of salts with different chemical compositions. However, so far only a small fraction of these ABW structures have

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been recognized and tabulated. In this paper, a much more comprehensive list of salts isotypic to the ABW framework is presented. This expanded tabulation reveals that the zeolite framework could be constructed from a much broader array of chemical compositions. Novel systems include sulfate and chromate zeolites with monovalent (T^+) and hexavalent (T^{6+}) tetrahedral centers. The finding of two fluoroberyllates with a zeolite-type topology further expands the compositional limit for a zeolite structure. This work is thus important for the future design of new zeolite materials with novel framework compositions.

EXPERIMENTAL

Synthesis

To synthesize NH_4ZnPO_4(I) with an ABW structure, $Zn(NO_3)_2 \cdot 6H_2O$ (2.00 g), ethylene glycol (15.80 g), 85% H_3PO_4 (1.66 g), and $(C_6H_{10})(NH_2)_2$ (1,2-diaminocyclohexane, the NH_4^+ source) (1.28 g) were sealed in a Teflon-coated steel autoclave, which was then heated at 180°C for 8 d. The product was recovered by filtration and washed with deionized water. Translucent irregular-shaped crystals with a typical dimension of 200 μm in length were obtained. The crystal used for single-crystal X-ray diffraction was both rotation and inversion twinned.

To synthesize NH_4ZnPO_4 (II) with an ABW structure free from rotation twinning, $Zn(NO_3)_2 \cdot 6H_2O$ (0.794 g), distilled water (6.326 g), 85% H_3PO_4 (1.07 g), and 6 *M* NH_4OH (31.25 g) were sealed in a Teflon-coated steel autoclave, which was then heated at 140°C for 6 d. The product was recovered by filtration and washed with deionized water. Translucent irregular-shaped crystals with a typical dimension between 200 to 300 μm in length were obtained. The needle-shaped hexagonal NH_4ZnPO_4 polymorph isostructural to NH_4CoPO_4-HEX[9] was also found in the product mixture.

To synthesize NH_4BePO_4 with an ABW structure, $Be(OH)_2$ (0.252 g), $NH_4H_2PO_4$ (2.30 g), 4 *M* H_3PO_4 (3.00 g), and distilled water (2.00 g) were mixed and heat-sealed in a Teflon pouch. The mixture was treated hydrothermally at 175°C for 4 d. The product was recovered by filtration and washed with deionized water. Clear needle crystals with a typical dimension of 400 μm in length were obtained.

Elemental analysis and thermal analysis

The elemental analysis was performed by Microanalytical Laboratory (University of California, Berkeley) on NH_4ZnPO_4(I) prepared from 1,2-diaminocyclohexane to verify the presence of NH_4^+. The calculated values (in mass percent) are 7.85 N and 2.26 H; experimental values are 7.67 N, 2.32 H.

NH_4ZnPO_4 (I) (49.7 mg) prepared from 1,2-diaminocyclohexane and NH_4BePO_4 (49.3 mg) were used in thermogravimetric analysis (TGA) and differential thermal analysis (DTA), which were performed on a Netzsch Simultaneous Thermal Analysis (STA) 409 system in static air with a heating rate of 5°C/min, from 30 to 1000°C. For NH_4ZnPO_4, up to 1000°C, there was only one single-step weight loss of 14.5% between 300 and 450°C, accompanied by a large endothermic peak. After the weight loss, the DTA showed no significant thermal events until 1000°C. For NH_4BePO_4, there was also only one single-step weight loss of 21.7% accompanied by a large endothermic peak, but it occurred between 500 and 610°C, significantly higher than that for NH_4ZnPO_4. After the weight loss, the DTA showed no significant thermal events up to 1000°C. Assuming the formation of $Zn_2P_2O_7$ and $Be_2P_2O_7$, the calculated weight loss is 14.6% for NH_4ZnPO_4 and 21.3% for NH_4BePO_4, in good agreement with the observed values.

Single-crystal structure determination

Crystallographic results are summarized in *Table 1*, while the atomic coordinates, selected bond distances, and angles are listed in *Tables 2* and *3*, respectively. ORTEP drawings of asymmetric units for two structures are shown in *Figure 1*.

Crystals were glued to thin glass fibers with epoxy resin and mounted on a Siemens Smart CCD diffractometer equipped with a normal-focus, 2.4 kW sealed-tube X-ray source (Mo*K*α radiation, λ = 0.71073Å) operating at 50 kV and 40 mA. About 1.3 hemisphere of intensity data were collected in 1321 frames with ω scans (width of 0.30° and exposure time of 30 sec per frame). Unit cell dimensions of NH_4ZnPO_4 (I) were determined by a least-squares fit of 2441 [2453 for NH_4ZnPO_4 (II) and 2454 for NH_4BePO_4] reflections with $I > 10\sigma(I)$ and $10° < 2\theta < 56°$. The empirical absorption corrections were based on the equivalent reflections, and other possible effects such as absorption by the glass fiber were simultaneously corrected. The structures were 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 and included secondary extinction corrections and anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms for NH_4ZnPO_4 were not included in the refinement owing to the orientational disorder of two NH_4^+ groups. However, the presence of NH_4^+ was verified by the elemental analysis. Hydrogen atoms for NH_4BePO_4 were located from the difference Fourier map and refined isotropically. Parameter shifts in the final least-squares cycle were smaller than 0.03σ.

RESULTS AND DISCUSSION

Synthesis conditions

An important observation in the syntheses of two ammonium ABW structures is that significantly different amines can be used as the source for the extra-framework NH_4^+ cations. It has been found that when different amines such as NH_4^+, $(CH_3)_4N^+$, $(CH_3CH_2CH_2)_3N$, and 1,4-diazabicyclo[2.2.2]octane (DABCO, $C_6H_{12}N_2$) are used as templates in the aqueous beryllophosphate syntheses at 200°C in Teflon pouches, only NH_4BePO_4 is recovered after 4 d at neutral pH. This result implies

Table 1 Summary of crystal data and refinement results

Structural formula	NH_4ZnPO_4 (I)	NH_4ZnPO_4 (II)	NH_4BePO_4
Formula weight	178.38	178.38	122.02
Color and habit	clear plate	clear prism	clear needle
Crystal size (mm^3)	0.20 × 0.12 × 0.04	0.16 × 0.14 × 0.12	0.24 × 0.067 × 0.033
a(Å)	8.8039(2)	8.7966(5)	8.7196(7)
b(Å)	5.4477(1)	5.4565(3)	8.5919(7)
c(Å)	8.9812(1)	8.9654(5)	4.9661(4)
β(°)	90.092(2)	90.323(1)	90
V(Å^3)	430.75(1)	430.32(4)	372.05(5)
Z	4	4	4
Space group	$P2_1$(No. 4)	$P2_1$(No. 4)	$Pna2_1$(No. 33)
ρ_{calc} (g/cm^3)	2.751	2.753	2.178
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073
μ(Mo Kα) (mm^{-1})	5.964	5.970	0.608
Maximum θ (°)	28.30	28.00	28.23
Unique data	1838	1862	1838
Parameters	131	129	81
$R(F)^a$	3.86%	3.81%	2.37(2)
$R_w(F^2)^b$	9.89%	9.35%	5.44%
GOF	1.06	1.06	1.04

NH_4ZnPO_4-ABW (I) and NH_4ZnPO_4-ABW (II) have the same structure, but are twinned differently. Note the difference in the unit cell β angle.

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

[b] $R(F^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ with $F_o > 4.0\sigma(F)$. $w = 1/[\sigma^2(F_o^2) + (A*P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. A = 0.0724 for NH_4ZnPO_4 (I); A = 0.0548 for NH_4ZnPO_4 (II); A = 0.0333 for NH_4BePO_4.

hydrolysis of many nitrogen-containing templates to NH_4^+ at typical zeolite synthesis conditions.

We have previously observed that the twinning habit of the NH_4CoPO_4 ABW phase is affected by the NH_4^+ source.[9] The similar effect is also observed here in the synthesis of the NH_4ZnPO_4 ABW phase. When NH_4OH is used in place of 1,2-diaminocyclohexane as the NH_4^+ source, we are able to eliminate the rotation twinning found in crystals prepared from 1,2-diaminocyclohexane. But the use of NH_4OH leads to a mixture of NH_4ZnPO_4-ABW and NH_4ZnPO_4-HEX phases similar to that found in the synthesis of the NH_4CoPO_4 ABW phase.[9]

Table 2 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3)

	x	*y*	*z*	U_{eq}[a]
NH_4ZnPO_4 (II)				
Zn(1)	6748(1)	−6762(1)	962(1)	13(1)
Zn(2)	1752(1)	−6381(1)	4205(1)	13(1)
P(1)	−1957(1)	−6412(3)	4276(2)	11(1)
P(2)	3044(2)	−6733(3)	935(1)	10(1)
N(1)	−22(6)	−6496(13)	8029(6)	22(1)
N(2)	5010(6)	−1773(12)	3113(6)	22(1)
O(1)	7267(5)	−4459(8)	−611(5)	19(1)
O(2)	8069(5)	−5920(10)	2615(5)	25(1)
O(3)	4645(4)	−6392(12)	1586(5)	23(1)
O(4)	2854(5)	−5221(8)	−502(5)	18)1)
O(5)	1880(5)	−5839(8)	2078(5)	18(1)
O(6)	−327(4)	−6558(10)	4887(4)	17(1)
O(7)	−2798(5)	−4322(8)	5107(6)	19(1)
O(8)	2785(5)	−3822(8)	5372(5)	18(1)
NH_4BePO_4				
P(1)	8166(1)	9146(1)	8410(1)	7(1)
Be(1)	11740(2)	9076(2)	8489(25)	9(1)
O(1)	9892(1)	8924(2)	8479(6)	17(1)
O(2)	7650(2)	9640(2)	5589(3)	11(1)
O(3)	7674(2)	10421(2)	10431(4)	12(1)
O(4)	7384(2)	7630(1)	9191(3)	14(1)
N(1)	5048(2)	8080(2)	3466(6)	18(1)
H(1)	5914(27)	8727(27)	3910(68)	25(7)
H(2)	4081(33)	8562(33)	3707(109)	50(8)
H(3)	5091(31)	7105(47)	4625(71)	45(10)
H(4)	5080(35)	7933(38)	1820(77)	33(10)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Description of the ABW structure

The framework of NH_4ZnPO_4 and NH_4BePO_4 has the same topology as that of zeolite ABW-type structures (*Figure 2*).[13] The ABW framework can be considered as built either from the stacking of 4.8^2 nets or hexagonal layers (6^3 nets). The latter view allows easy comparisons with the structure of tridymite. The difference between the tridymite and ABW structures lies in the way hexagonal layers are joined together with the oxygen bridges. Such a difference gives rise to eight-ring channels in the ABW framework and six-ring channels in the tridymite framework. In tridymite, each hexagonal ring consists of tetrahedral atoms pointed up and down alternatively (UDUDUD), while in a zeolite ABW structure, each hexagonal ring has three adjacent tetrahedral atoms all directed up with the other adjacent three all directed down (UUUDDD). Because of the similarity between the tridymite and the ABW framework, structures with the ABW-type framework have sometimes been classified as belonging to the stuffed tridymite family in the literature. For example, the ABW phase $CsBeAsO_4$ was reported to be in the tridymite family rather than in the ABW family.[14]

Similar hexagonal layers are found in a number of important aluminosilicate zeolite frameworks such as mordenite and ferrierite. However, unlike zeolite ABW-type structures, hexagonal layers in these zeolites are not directly connected with a single oxygen layer, but

Table 3 Selected bond lengths (Å) and angles (°)

NH_4ZnPO_4 (II)			
Zn(1)–O(2)	1.934(4)	Zn(1)–O(1)	1.945(4)
Zn(1)–O(3)	1.947(4)	Zn(1)–O(4)	1.964(4)
Zn(2)–(5)	1.933(4)	Zn(2)–O(6)	1.934(4)
Zn(2)–O(7)	1.949(4)	Zn(2)–O(8)	1.964(4)
P(1)–O(2)	1.513(5)	P(1)–O(6)	1.534(4)
P(1)–O(8)	1.537(5)	P(1)–O(7)	1.552(5)
P(2)–O(3)	1.532(4)	P(2)–O(5)	1.533(4)
P(2)–O(4)	1.538(4)	P(2)–O(1)	1.540(4)
O(2)–Zn(1)–O(1)	105.1(2)	O(2)–Zn(1)–(3)	108.8(2)
O(1)–Zn(1)–O(3)	111.6(2)	O(2)–Zn(1)–O(4)	106.4(2)
O(1)–Zn(1)–O(4)	115.2(2)	O(3)–Zn(1)–O(4)	109.3(2)
O(5)–Zn(2)–O(6)	112.4(2)	O(5)–Zn(2)–O(7)	114.1(2)
O(6)–Zn(2)–O(7)	107.7(2)	O(5)–Zn(2)–O(8)	112.8(2)
O(6)–Zn(2)–O(8)	107.6(2)	O(7)–Zn(2)–O(8)	101.5(2)
O(2)–P(1)–O(6)	110.0(2)	0(2)–P(1)–O(8)	111.3(3)
O(6)–P(1)–O(8)	109.0(3)	O(2)–P(1)–O(7)	110.6(3)
O(6)–P(1)–O(7)	108.3(3)	O(8)–P(1)–O(7)	107.6(2)
O(3)–P(2)–O(5)	108.8(3)	O(3)–P(2)–O(4)	110.5(3)
O(5)–P(2)–O(4)	108.6(3)	O(3)–P(2)–O(1)	110.6(3)
O(5)–P(2)–O(1)	108.3(3)	O(4)–P(2)–O(1)	110.0(3)
P(2)–O(1)–Zn(1)	135.9(3)	P(1)–O(2)–Zn(1)	134.5(3)
P(2)–O(3)–Zn(1)	138.6(3)	P(2)–O(4)–Zn(1)	132.2(3)
P(2)–O(5)–Zn(2)	130.8(3)	P(1)–O(6)–Zn(2)	140.2(3)
P(1)–O(7)–Zn(2)	122.1(3)	P(1)–O(8)–Zn(2)	119.9(3)
NH_4BePO_4			
P(1)–O(1)	1.5171(11)	P(1)–O(4)	1.5203(13)
P(1)–O(2)	1.531(2)	P(1)–O(3)	1.547(2)
Be(1)–O(4)	1.608(3)	Be(1)–O(2)	1.609(8)
Be(1)–O(1)	1.616(2)	Be(1)–O(3)	1.660(10)
N(1)–H(1)	0.96(3)	N(1)–H(2)	0.95(3)
N(1)–H(3)	1.02(4)	N(1)–H(4)	0.83(4)
O91)–P(1)–O(4)	109.37(8)	O(1)–P(1)–O(2)	110.3(2)
O(4)–P(1)–O(2)	109.81(9)	O(1)–P(1)–O(3)	110.46(12)
O(4)–P(1)–O(3)	108.46(13)	O(2)–P(1)–O(3)	108.39(10)
O(4)–Be(1)–O(2)	111.6(6)	O(4)–Be(1)–O(1)	106.0(2)
O(2)–Be(1)–O(1)	112.8(4)	O(4)–Be(1)–O(3)	109.2(4)
O(2)–Be(1)–O(3)	108.2(2)	O(1)–Be(1)–O(3)	109.0(5)
P(1)–O(1)–Be(1)	168.12(12)	P(1)–O(2)–Be(1)	133.3(3)
P(1)–0(3)–Be(1)	133.84(13)	P(1)–O(4)–Be(1)	151.9(4)
H(1)–N(1)–H(2)	115(2)	H(1)–N(1)–H(3)	109(2)
H(2)–N(1)–H(3)	109(3)	H(1)–N(1)–H(4)	107(3)
H(2)–N(1)–H(4)	103(4)	H(3)–N(1)–H(4)	116(3)

rather with Al and Si oxygen tetrahedral clusters.[15] This may involve five-membered rings (five tetrahedral atoms in a ring). This is not possible in zincophosphates or other divalent metal phosphates because of the requirement for the strict alternation of different tetrahedral centers.

It should be noted that NH_4ZnPO_4 has the monoclinic symmetry (space group: $P2_1$) while NH_4BePO_4 has the orthorhombic symmetry (space group: $Pna2_1$). Both space groups are typical of zeolite ABW structures.[13] Because ABW structures are typically non-centrosymmetric and are capable of a variety of chemical substitutions similar to those structures in the KTP[16] (KTP = potassium titanyl phosphate) family, a systematic study of the ABW family of salts with various chemical compositions can lead to materials with useful electro-optic properties such as second harmonic generation (SHG).

Hydrogen bonding

The ammonium cations in NH_4ZnPO_4 and NH_4BePO_4 are located at the center of six-ring channels rather than at the center of eight-ring channels.

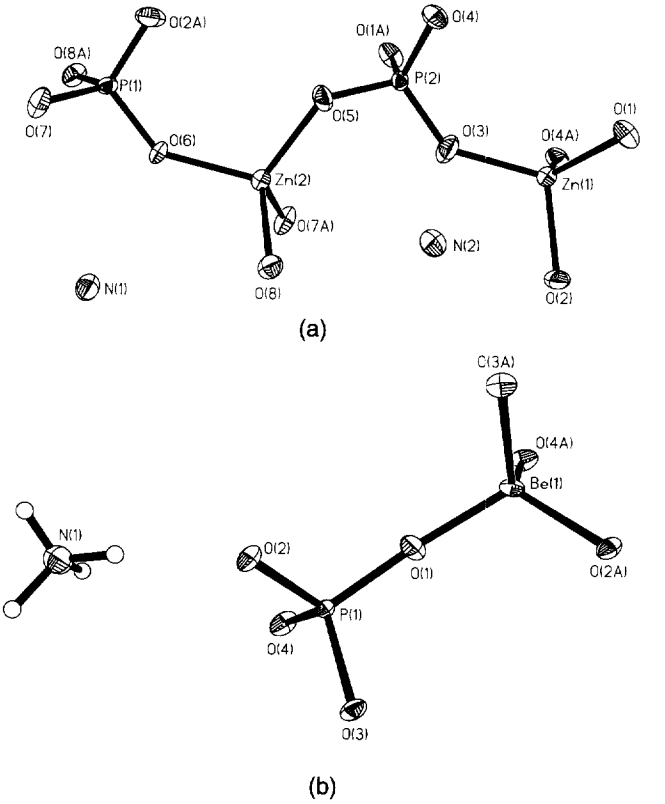

Figure 1 An ORTEP (50%) drawing showing local coordination environment. Atoms with labels containing "A" and "B" are symmetry generated. (a) The asymmetric unit contains two NH_4ZnPO_4 formula units. (b) The asymmetric unit contains one NH_4BePO_4 formula unit.

This arrangement is able to provide enough cationic sites to balance the negative charge of the framework. In agreement with the different symmetry of the two crystals, there are two unique ammonium sites in NH_4ZnPO_4 and only one unique ammonium site in NH_4BePO_4.

For NH_4ZnPO_4, when viewed along the six-ring channel (the *a*-axis), two crystallographically different nitrogen atoms alternate along the channel direction. However, when viewed along the eight-ring channel (the *b*-axis), nitrogen atoms of the same type are in the same eight-ring channel (*Figure 2*). Nitrogen atoms in NH_4ZnPO_4 are relatively close to the framework oxygen atoms, with the closest distances of 2.828(6)Å for N1–O6 and 2.856(7)Å for N2–O7 calculated using coordinates for NH_4ZnPO_4 (II). This indicates that hydrogen bonds (N–H . . . O) exist between NH_4^+ and framework oxygen atoms. However, despite such directed hydrogen bonds, the NH_4^+ cations have more than one statistical orientation. All prominent residual electron density peaks are around the nitrogen atoms, but they do not form a well-defined tetrahedra. This suggests that NH_4^+ cations might be slightly too small for the $ZnPO_4$ ABW framework and are orientationally disordered. The similar orientational disorder was also observed in the NH_4CoPO_4 ABW phase.[9]

The ammonium cation in NH_4BePO_4 is completely

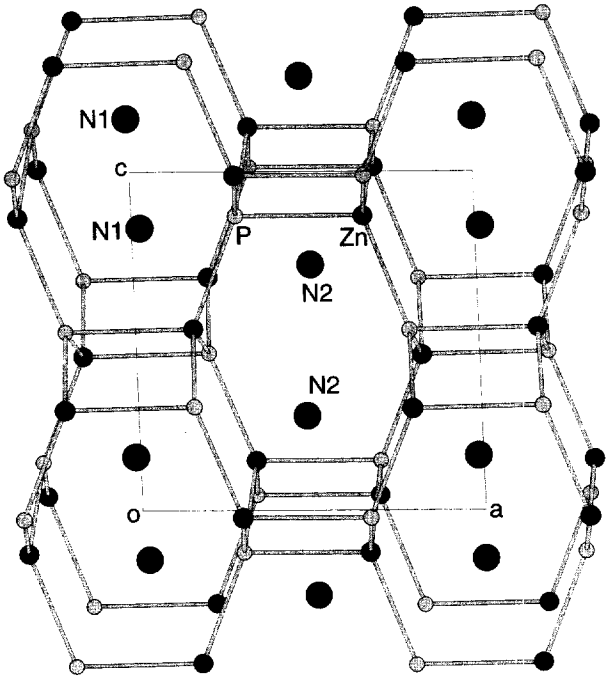

Figure 2 The eight-ring channel in the ZnPO ABW framework viewed along the *b* axis. The hexagonal layers are stacked from left to right (the crystallographic *a* axis). Four such layers are shown. Unconnected circles represent nitrogen atoms.

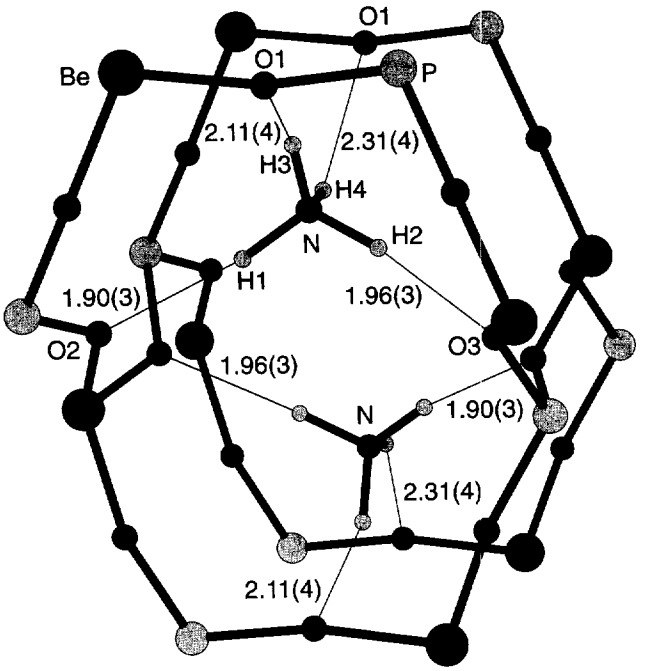

Figure 3 Hydrogen bonds shown as single lines between NH_4^+ and framework oxygen sites. Two eight-rings joined by two oxygen atoms are shown. The numbers are O–H distances in angstroms.

ordered so that all four hydrogen atoms can be easily located and refined. The substitution of Be^{2+} for Zn^{2+} or Co^{2+} leads to a significantly smaller unit cell volume (372.1Å^3 for $BePO_4$, 430.7Å^3 for $ZnPO_4$, and 432.9Å^3 for $CoPO_4$) and channels that restrict the motion of NH_4^+ in channels of the $BePO_4$ framework. Hydrogen bonds between NH_4^+ and framework oxygen atom sites in NH_4BePO_4 are depicted in *Figure 3*. All hydrogen atoms are involved in hydrogen bonds, which contribute to the total ordering of NH_4^+ cations. These hydrogen bonds may have played a structure-directing role in the formation of the $BePO_4$ ABW framework.

Twinning and pseudosymmetry

Like hydrated Li-ABW phases, NH_4BePO_4 has an orthorhombic symmetry. From the unit cell parameters and intensities of reflections, NH_4ZnPO_4 (I) also appeared to have the orthorhombic symmetry. However, attempts to solve the structure in orthorhombic space groups were unsuccessful. It was suspected that NH_4ZnPO_4 (I) might be monoclinic, but was rotation twinned so that the intensity data and cell parameters appeared to be orthorhombic. The structure was then solved in $P2_1$. The intensity data of NH_4ZnPO_4 (II) did not emulate the orthorhombic symmetry as it was only an inversion twin.

The crystal of NH_4ZnPO_4 (I) has four twin domains. In addition to the inversion twinning, the crystal is also a rotation twin that involves the reversal of *b* and *c* axes. The structural refinements without taking into account of rotation twinning give poor agreement factors. Significantly better results are obtained when the twinning is refined (*Table 4*). The refinement results show that there is an excess of one enantiomorph (*Table 5*). The presence of the rotation twinning leads to a deviation of the unit cell β angle from its true value.

In comparison, the crystal of NH_4ZnPO_4 (II) is only inversion twinned and consists of two domains. There is a large excess of one enantiomorph over the other (*Table 5*). The absence of rotation twinning allows the accurate determination of the unit cell parameters, particularly the β angle. The β angle obtained from NH_4ZnPO_4 (II) (90.32°) is in better agreement with that derived form the powder diffraction data. The unit cell parameters from powder data were previously reported as the following: a = 8.960Å, b = 5.438Å, c = 8.781Å, β = 90.35°.[17] The effect of twinning on the observed unit cell parameters from single-crystal diffraction has been previously reported for the NH_4CoPO_4 ABW phase.[9] Note that cell parameters refined from powder data are not affected by twinning.

Thermal stability

Three ammonium ABW salts (NH_4CoPO_4, NH_4ZnPO_4, and NH_4BePO_4) have been discovered so far. The thermal analysis shows that the loss of NH_3 molecules during heating in air is accompanied simultaneously by the loss of water molecules, which leads to

Table 4 Comparison of refinement results with and without refining twinning

NH_4ZnPO_4 (I)	R(F)	wR(F^2)	GOF
Twinning not refined	11.60%	29.98%	1.13
Twinning refined	3.86%	9.89%	1.06

Table 5 Summary of the percentage of twin domains in NH_4ZnPO_4 (I) and NH_4ZnPO_4 (II)

	Component: A	Rotation twin of A: B	Racemic twin of A: C	Rotation and racemic twin of A: D	Enantiomorph ratio (A + B vs. C + D)
NH_4ZnPO_4 (I)	0.18(3)	0.21(3)	0.41(3)	0.20(3)	0.39:0.61
NH_4ZnPO_4 (II)	0.16(2)	—	0.84(2)	—	0.16:0.84

There are four twin domains related by the inversion center and the two-fold twin axis in NH_4ZnPO_4 (I). Two domains related by the twin axis have the same absolute configuration.

the collapse of the ABW framework. Other means may have to be exploited to investigate if ammonia could be removed while maintaining the framework structure. The onset decomposition temperature of these salts indicates that the thermal stability is the following: $NH_4BePO_4 > NH_4ZnPO_4 \approx NH_4CoPO_4$. The relatively high thermal stability of NH_4BePO_4 may be related to the presence of strong hydrogen bonds described above. The thermal properties of ammonium salts are unique compared to some other anhydrous ABW salts, which show displacive phase transitions as discussed below.

Cation size effect on the framework type

A number of zinc phosphates with the formula $MZnPO_4$ (M = Li^+, Na^+, K^+, Rb^+, Cs^+, Tl^+ . . .) are known. The structure type of these salts depends on the size of cations in an analogous way as those observed for cobalt phosphates[9] and aluminosilicates.[18] As expected from the consideration of ionic radii, NH_4ZnPO_4 is isostructural to $TlZnPO_4$, $RbZnPO_4$, and $CsZnPO_4$. This indicates that the ABW-type structure is the stable framework for large cations. For smaller cations, several different structural types provide better fit. A summary of $MZnPO_4$ and $MBePO_4$ salts that show the cation size effect is given in *Table 6*.

One important difference exists between aluminosilicates and divalent metal phosphates: No cobalt or zinc phosphates have been found to possess the tridymite or quartz-type frameworks observed in aluminosilicates, and no aluminosilicates possess the ABW-tridymite hybrid framework.[9] One interesting observation is that neither $KZnPO_4$ nor $KCoPO_4$ adopts the ABW topology (*Table 6*) because the potassium cation is too small for $ZnPO_4$ and $CoPO_4$ ABW frameworks. However, when the ABW framework was compressed with the substitution of ZN^{2+} or Co^{2+} by Be^{2+}, the size of the potassium cation would match the cage size offered by the $BePO_4$ ABW topology. That is why $KBePO_4$ has an ABW structure, whereas $KZnPO_4$ and $KCoPO_4$ have the hybrid-type topology.

Other ABW structures

Compared to other zeolite structures, the ABW type is a relatively dense phase and is probably a thermodynamically stable phase in the presence of large extra-framework metal cations. Thus, various ABW-type structures with different chemical compositions have been found even though some of these were not related to the Li-A(BW) topology in the original reports. Some of these phases were synthesized using methods involving high temperature or even high pressure. This is in contrast with low-temperature hydrothermal methods typically used in the synthesis of metastable zeolite phases. It should be noted that some ABW phases were synthesized and characterized because of possible ferroelectric properties of these materials.[19]

So far, only 12 phases with different chemical compositions have been tabulated.[13] In *Table 7* we provide a much expanded list of zeolite ABW phases. These new additions give important insight into structural features and compositional diversity of ABW phases. All new additions were selected based on chemical formula, unit cell parameters, and space groups. In addition, the molecular modelling software was used to verify the framework topology of a possible candidate.[20]

Efforts to substitute tetrahedral atoms in the T^{3+}/T^{4+} zeolites with other charge combinations of tetrahedral atoms have resulted in tremendous successes in T^{2+}/T^{5+} and T^{3+}/T^{5+} systems. However, very little is

Table 6 Structural types of $MZnPO_4$ and $MBePO_4$ (M is a monovalent cation) as compared with similar cobalt phosphates and aluminosilicates

Structural types	$MZnPO_4$	$MBePO_4$	$MCoPO_4$[9]	$MAlSiO4$[18]
Phenakite	$LiZnPO_4$[23]	—	—	$LiAlSiO_4$
Cristobalite	$LiZnPO_4$[24,25]	—	—	$NaAlSiO_4$
Beryllonite	$NaZnPO_4$[26]	$NaBePO_4$[27]	—	$NaAlSiO_4$
ABW-tridymite hybrid	H_3OZnPO_4[a,28]	—	$NaCoPO_4$	—
	$KZnPO_4$[29]		$KCoPO_4$	
			NH_4CoPO_4-HEX	
ABW	NH_4ZnPO_4-ABW	$KBePO_4$	NH_4CoPO_4-ABW	$TlAlSiO_4$
	$TlZnPO_4$[30]	$CsBePO_4$	$RbCoPO_4$	$RbAlSiO_4$
	$RbZnPO_4$[31]			$CsAlSiO_4$
	$CsZnPO_4$[21]			

[a] Comparisons between ammonium zinc phosphates and ammonium cobalt phosphates suggest that $(H_3O)ZnPO_4$ is most likely an ammonium salt, not a hydronium salt as was originally reported.

Table 7 Summary of ABW structures with different chemical compositions and crystallographic symmetries

Formula[a]	Space group[b]	a	b	c	α/β/γ
Phosphates	T^{2+}/T^{5+}				
$LiBePO_4H_2O$[7,32]	$Pna2_1$	9.680(2)	7.8114(15)	4.758(1)	—
$KBePO_4$[33,34]	$Pna2_1$	8.30(2)	8.47(2)	5.00(2)	—
$RbBePO_4$[34]	$Pna2_1$	8.587(3)	8.636(3)	5.012(2)	
NH_4BePO_4	$Pna2_1$	8.7196(7)	8.5919(7)	4.9661(4)	—
$CsBePO_4$[34]	$Pnma$	8.713(4)	5.147(4)	8.836(5)	—
$RbCoPO_4$[13,9]	$P2_1$	8.8377(8)	5.4150(5)	8.9723(8)	90.212(2)
NH_4CoPO_4[9]	$P2_1$	8.7968(7)	5.4621(4)	9.0105(7)	89.983(2)
$LiZnPO_4H_2O$[7,25]	$Pna2_1$	10.575(2)	8.0759(9)	4.9937(6)	—
$TlZnPO_4$[30]	$P2_1$	8.732(2)	5.468(1)	8.841(2)	90.6
NH_4ZnPO_4	$P2_1$	8.8039(2)	5.4477(1)	8.9812(1)	90.092(2)
$RbZnPO_4$[31]	$P2_1$	8.855(3)	5.408(1)	8.956(4)	90.9
$CsZnPO_4$ (I)[21]	$Pnma$	9.194(3)	5.490(2)	9.388(4)	—
$CsZnPO_4$ (II)[21]	$Pna2_1$	9.236(6)	9.342(7)	5.462(3)	—
$CsZnPO_4$ (III)[21]	$P2_1/a$	18.54(9)	5.45(4)	9.10(3)	90.29(5)
Arsenates	T^{2+}/T^{5+}				
$LiBeAsO_4H_2O$[35]	$Pna2_1$	10.0416(4)	8.0285(3)	4.8553(2)	—
$LiZnAsO_4H_2O$[7]	$Pna2_1$	10.816	8.289	5.156	—
$TlBeAsO_4$[36]	$Pna2_1$	9.743(6)	8.213(6)	4.912(2)	—
$CsBeAsO_4$[14]	$Pna2_1$	9.342(4)	8.821(5)	5.166(2)	—
$TlZnAsO_4$[30]	$P2_1$	8.921(3)	5.631(1)	8.958(3)	91.03(2)
Sulfates	T^{+}/T^{6+}				
NH_4LiSO_4[37]	$P2_111$	5.277(2)	8.984(4)	8.656(3)	90.3
NH_4LiSO_4[38]	$P112_1/a$	17.511(6)	9.130(6)	5.274(2)	90.0
NH_4LiSO_4[38]	$P112_1/a$	8.786(6)	9.140(7)	5.280(2)	—
$N_2H_5LiSO_4$[40]	$Pna2_1$	9.929(5)	8.973(3)	5.181(2)	—
$RbLiSO_4$[41]	$P112_1/n$	5.288(1)	9.105(1)	8.731(1)	90.1
$CsLiSO_4$[42]	$P112_1/n$	9.379(2)	5.423(1)	8.834(3)	89.4
$CsLiSO_4$[42]	$Pnma$	8.820(3)	5.456(1)	9.456(2)	—
Silicates	T^{3+}/T^{4+}				
$LiAlSiO_4H_2O$[13]	$Pna2_1$	10.313(1)	8.194(1)	4.993(1)	—
$TlAlSiO_4$[13]	$Pna2_1$	8.297(1)	9.417(1)	5.413(1)	—
$RbAlSiO_4$[13]	$Pna2_1$	8.74(1)	9.22(6)	5.33(7)	—
$CsAlSiO_4$[13]	$Pna2_1$	8.907(2)	9.435(1)	5.435(1)	—
$LiGaSiO_4H_2O$[13]	$Pna2_1$	10.461	8.217	5.037	—
Miscellaneous					
$CsAlTiO_4$[21]	Imma	8.978(4)	5.740(1)	9.969(2)	—
$CsLiCrO_4$[43,44]	$P112_1/b$	9.744(2)	5.636(1)	8.956(3)	90.4
$N_2H_5LiBeF_4$[45]	$Pna2_1$	9.811(4)	8.880(8)	5.139(4)	—
$CsLiBeF_4$[46]	$P112_1/n$	9.306(1)	5.383(1)	8.738(1)	89.8

[a] Except $RbBePO_4$ and $LiZnAsO_4 \cdot H_2O$, all other structures were refined using single crystal or powder data. Other possible ABW structures such as $RbMgPO_4$, $CsMgPO_4$, $KCoPO_4$, $TlCoPO_4$, and $CsCoPO_4$,[47] for which no structural refinements were indicated, are not listed. Some refined structures including $CsMnPO_4$[48] and one polymorph of $CsLiSO_4$[49] are not listed because of the disorder of framework oxygen sites.

[b] For $Pna2_1$ (No. 33) and *Pnma* (No. 62), there are five nonstandard settings ($Pc2_1n$, $P2_1cn$, $Pbn2_1$, $P2_1nb$, *and* $Pn2_1a$; *Pmnb, Pbnm, Pcmn, Pmcn,* and *Pnam*. Some salts were originally reported in nonstandard settings. We have transformed them into standard settings in most cases. However, for monoclinic cells, nonstandard settings are occasionally prefered as they show the pseudo-orthorhombic symmetry and can be conveniently compared to orthorhombic phases. The unit cell angles in the table refer to either α, β, or γ depending on the cell choice.

known about zeolites built from tetrahedral atoms with +1 and +6 charges. Sulfate and chromate ABW phases listed here are of particular interest as they suggest that it might be possible to synthesize new zeolite structures from monovalent tetrahedral cations (T^+ such as Li^+, Cu^+) and hexavalent tetrahedral cations (T^{6+} such as S^{6+}, Se^{6+}, Cr^{6+}, Mo^{6+}). One advantage of the T^+/T^{6+} system is that synthesis reactions and the crystal growth can usually be performed at ambient conditions.

Table 7 helps to predict new ABW phases in a systematic way. This can be useful as these $ABCX_4$ phases are typically noncentrosymmetric and could have potential uses as ferroelectric and nonlinear optical materials. The availability of the same type structure with various chemical compositions would allow the fine-tuning of some useful physical properties.

Lattice symmetry of ABW framework

The highest symmetry for the ABW-type framework topology is Imma. Thus, the ABW-type framework is also referred to as Icmm-type (Imma is the standard setting.) The Imma symmetry has only been realized in the crystal structure of $CsAlTiO_4$,[21] in which Al and Ti are statistically disordered so that it is not possible to distinguish between Al and Ti sites. The possible reason for such a disorder is the similar ionic radii between tetrahedral Al and Ti cations (Shannon-Prewitt radii: 0.39Å for Al^{3+} and 0.42Å for Ti^{4+}).

Other space groups that have been found in ABW

structures are *Pnma*, $Pna2_1$, $P2_1/c$, and $P2_1$ with $Pna2_1$ and $P2_1$ being the two most popular space groups at room temperature. Excluding cesium salts, all ordered ABW structures have space groups of either $Pna2_1$ or $P2_1$, both of which are noncentric. The polymorph III of $CsZnPO_4$ has twice the unit cell volume as do other ABW compounds. This is caused by the doubling of the *a*-axis, which is coincident with the stacking direction of hexagonal layers.

Of all ABW structures, the most important symmetry element is the two-fold screw axis. Such a screw axis is preserved in all known ABW structures. In nearly all ABW structures, the screw axis is aligned along the eight-ring channel direction, which is always the shortest crystallographic axis, with the axial length between 4.7 to 5.7Å. Exceptions are some sulfates and chromates, in which the two-fold screw axis is aligned along the stacking direction of hexagonal layers. Thus, the lowest symmetry for ABW structures is the chiral space group $(P2_1)$ in the monoclinic system. However, the unit cells of all ABW phases are orthogonal or nearly orthogonal.

When the deviation of the β angle from the ideal 90° is small, there is a tendency for a monoclinic ABW crystal to be twinned to emulate orthorhombic symmetry. In addition to such a twinning, ABW structures in chiral space groups are also subject to the inversion twinning. Because ABW crystals can in theory be either orthorhombic or monoclinic, the pseudosymmetry resulting from the twinning could lead to some difficulties in the structure analysis when the twinning is not recognized.

Several phases have also been reported to have interesting phase transitions. The symmetry of the $CsZnPO_4$ ABW framework increases with temperature from $P2_1/c$ at room temperature to $Pna2_1$ at 280°C and *Pnma* at 340°C.[22] The similar displacive phase transition was also reported for $CsBeAsO_4$,[14] which underwent reversible-phase transition from low-temperature form $(Pna2_1)$ to the centric high-temperature form (*Pnam*) at 559°C. NH_4LiSO_4 has four phases with symmetry ranging from $P2_1$ to *Pnma*. Three of those phases (except the $P2_1$ phase) are similar to the corresponding $CsZnPO_4$ polymorphs.

CONCLUSIONS

We have described the syntheses, thermal stability, and structural features of two new ammonium ABW salts. One of them, NH_4ZnPO_4, is similar to the NH_4CoPO_4 ABW phase in almost all aspects including twinning and effects of synthesis conditions on the twinning. A number of examples are given to show the effect of cation size on the framework structure types, with a conclusion that large monovalent cations usually lead to the formation of the ABW topology. We have identified many more ABW structures not previously recognized. These novel ABW structures indicate that it might be possible to design new zeolite structures with a much broader array of chemical compositions.

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APPENDIX

X-ray Crystallography Data

Table A-1 Anisotropic displacement parameters ($A^2 \times 10^3$ for NH_4BePO_4

	U11	U22	U33	U23	U13	U12
P(1)	8(1)	5(1)	7(1)	0(1)	0(1)	0(1)
Be(1)	11(1)	8(1)	7(1)	4(2)	3(2)	0(1)
0(1)	10(1)	26(1)	16(1)	−1(1)	1(1)	2(1)
0(2)	16(1)	10(1)	8(1)	1(1)	−2(1)	−3(1)
0(3)	16(1)	9(1)	10(1)	−4(1)	−1(1)	3(1)
0(4)	21(1)	10(1)	11(1)	−1(1)	2(1)	−6(1)
N(1)	16(1)	19(1)	19(1)	−2(1)	1(1)	1(1)

Table A-2 Anisotropic displacement parameters ($A^2 \times 10^3$) for NH_4ZnPO_4 (II)

	U11	U22	U33	U23	U13	U12
Zn(1)	13(1)	13(1)	12(1)	0(1)	1(1)	0(1)
Zn(2)	13(1)	14(1)	13(1)	0(1)	2(1)	0(1)
P(1)	10(1)	12(1)	11(1)	−1(1)	−1(1)	−1(1)
P(2)	11(1)	9(1)	10(1)	−1(1)	2(1)	−1(1)
N(1)	21(2)	26(3)	18(2)	−4(3)	−1(2)	4(3)
N(2)	20(2)	25(3)	20(2)	−2(3)	2(2)	0(2)
0(1)	29(2)	11(2)	16(2)	3(2)	6(2)	7(2)
0(2)	30(2)	34(3)	11(2)	5(2)	−7(2)	−14(2)
0(3)	12(2)	31(3)	26(2)	−3(2)	−1(2)	1(2)
0(4)	25(2)	17(2)	13(2)	4(2)	2(2)	−1(2)
0(5)	17(2)	23(2)	14(2)	−2(2)	8(2)	8(2)
0(6)	12(2)	20(2)	18(2)	5(2)	−1(1)	3(2)
0(7)	13(2)	14(2)	30(3)	−9(2)	2(2)	0(2)
0(8)	17(2)	13(2)	24(3)	−6(2)	−2(2)	3(2)

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