Structures and Properties of New Zeolite X-Type Zincophosphate and Beryllophosphate Molecular Sieves

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The solid-state chemistry of non-aluminosilicate molecular sieves has recently undergone a renaissance, following the discovery of a number of aluminophosphate (AlPO)[1] and new gallosilicate (GaSiO)[2] phases a few years ago. Recently, several beryllophosphate (BePO)[3,4] materials have been reported. Some of these AlPOs, GaSiOs, and BePOs are isostructures of known aluminosilicates, while others are new framework topologies. We have recently prepared a number of zeolitic zincophosphates (ZnPOs), zincoarsenates (ZnAsOs), and berylloarsenates (BeAsOs) for the first time, extending the variety of framework compositions still further. In particular, the hypothetical beryllium/zinc phosphate/arsenate "framework" formula $((Be/Zn)O_2(P/As)O_2)^-$ is electronically equivalent with the aluminosilicate framework $(AlO_2SiO_2)^-$, as found in zeolites with a Si:Al ratio of 1:1. In this paper, we report the structures of new beryllophosphate (BePO–X) and zincophosphate (ZnPO–X) phases that are analogues of the industrially important zeolite-X framework. Their formulas are $Na_{96}(BePO_4)_{96}\cdot192H_2O$ and $Na_{67}TMA_{12}Zn_8(ZnPO_4)_{96}\cdot192H_2O$ (TMA = tetramethylammonium cation), respectively. Zeolite-X and zeolite-Y are synthetic isostructures of the mineral faujasite and have been widely studied by diffraction and other techniques, especially with respect to cation-exchange and molecular absorption properties.[5,6] Faujasite-type phases contain one of the largest pore openings of any known

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Table I. Final Atomic Coordinates for BePO–X (Cubic, Space Group $Fd\bar{3}$, a = 23.368 (2) Å)

atom	x	y	z	occ[a]	$100U_{iso}$
Be(1)	−0.0525 (6)	0.1247 (7)	0.0357 (6)		1.1 (2)
P(1)	−0.0547 (8)	0.0370 (8)	0.1226 (10)		1.1 (2)
O(1)	−0.1071 (6)	0.0071 (6)	0.1043 (6)		1.1 (2)
O(2)	−0.0066 (6)	−0.0013 (6)	0.1477 (4)		1.1 (2)
O(3)	−0.0279 (4)	0.0687 (7)	0.0694 (7)		1.1 (2)
O(4)	−0.0730 (5)	0.0768 (8)	0.1740 (7)		1.1 (2)
Na(1)	0	0	0	1.08 (7)	2.8 (6)
Na(2)	0.067 (2)	0.067 (2)	0.067 (2)	0.47 (4)	2.8 (6)
Na(3)	0.2442 (6)	0.2442 (6)	0.2442 (6)	1.04 (7)	2.8 (6)

a Fractional site occupancy.

zeolite (ca. 8 Å) and are of industrial importance for petroleum cracking and other reactions.[7]

Both the sodium BePO–X and sodium/tetramethylammonium ZnPO–X were prepared at ambient conditions, as described elsewhere;[8] for example, ZnPO–X can be synthesized in 30 min at 4 °C. Preliminary X-ray powder diffraction data revealed highly crystalline phases, which could be indexed as face-centered cubic cells with dimensions a = 23.383 (5) Å for BePO–X and a = 25.226 (5) Å for ZnPO–X, suggesting that these phases were related to aluminosilicate zeolite-X (a = ca. 25.03 Å). For ZnPO–X, high-resolution powder X-ray data were collected on a Scintag PAD X diffractometer operating in θ–θ geometry (λ = 1.541 78 Å), between 2θ = 20 and 80° by using 0.02° steps to give 3000 data points. For BePO–X, a 5-g sample was dehydrated under vacuum at 150 °C overnight, and low-temperature powder neutron diffraction data were measured by using the high-resolution, five-detector, powder diffractometer on beam line BT-1, at the National Institute of Standards and Technology (NIST), Gaithersburg, MD. The sample was enclosed in a cylindrical vanadium can, and the data were collected at 10 (1) K, using a neutron wavelength of 1.553 Å between 2θ = 5 and 120°, with a step size of 0.05°. Prior to analysis, the data were corrected for detector effects and collated.

Rietveld profile refinement was carried out with the program GSAS,[9] using the starting framework model of aluminosilicate zeolite-X as determined by Olson from single-crystal X-ray data,[10] in space group $Fd\bar{3}$ (No. 203). Our BePO–X and ZnPO–X models assumed a fully ordered 1:1 distribution of Be/Zn and P over the framework tetrahedra, and strict alternation of Be/Zn and P between adjacent tetrahedra, as would be the case for an X-type zeolite with a 1:1 Si:Al ratio, showing perfect cation alternation. For each phase, the usual profile parameters, including scale factor, detector zero-point correction, background coefficients, the unit-cell parameter and peak shape–width variation terms, and the framework-atom positional and isotropic thermal parameters, were refined. Before any guest species were included in the model, the profile R factor was over 30%. For BePO–X, sodium cations were positioned at the sites found in previous studies of dehydrated faujasite-type materials. For ZnPO–X, extraframework species were progressively located by difference Fourier syntheses and added to the refinement. The largest difference peaks were assigned to the guest sodium cation, and those remaining were assigned to extraframework water molecules. No reasonable geometry corresponding to the tetramethylammonium

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Table II. Selected Bond Distance (angstroms) and Angle (degrees) Data for BePO–X

Be(1)–O(1)	1.62 (3)	Be(1)–O(2)	1.64 (3)
Be(1)–O(3)	1.63 (3)	Be(1)–O(4)	1.55 (3)
P(1)–O(1)	1.47 (3)	P(1)–O(2)	1.55 (3)
P(1)–O(3)	1.58 (4)	P(1)–O(4)	1.58 (3)
Na(1)–O(3)	2.372 (8) × 6	Na(2)–O(3)	2.22 (3) × 3
Na(3)–O(2)	2.28 (2) × 3		
O–Be(1)–O^a	109 (2)	O–P(1)–O^a	110 (4)
Be(1)–O–P(1)^b	136 (2)		

^{a} Tetrahedral average. ^{b} Bridging oxygen average.

SODIUM BEPO–X   10K NBS DATA   NICOL/HARRISON
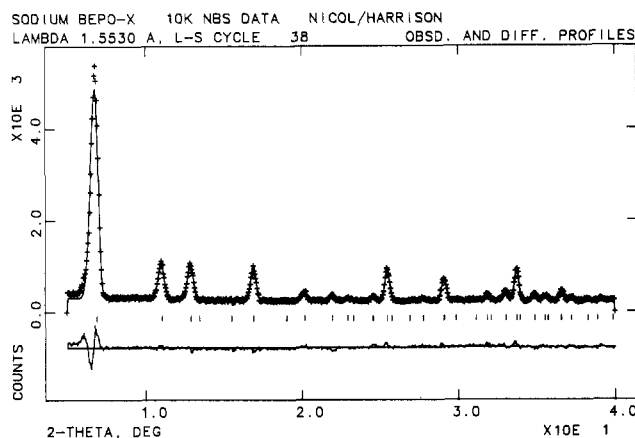LAMBDA 1.5530 A, L–S CYCLE   38   OBSD. AND DIFF. PROFILES

Figure 1. Final observed (crosses), calculated (line), and difference profile plots, with reflection positions indicated by tickmarks for BePO–X (first detector, low-angle neutron data).

(TMA) guest cation could be established. For both BePO–X and ZnPO–X, the occupancies and thermal factors of the guest sites were carefully refined to ensure convergence to the best possible minimum. The refinement of the ZnPO–X structure was significantly improved by including the water molecules, and T atom to oxygen (d(Zn–O) = 1.93 (1) Å, d(P–O) = 1.53 (1) Å) bond-length restraints were used to stabilize the refinement of the framework: their relative weights were progressively reduced as convergence was achieved. No bond-distance restraints were employed for the BePO–X refinement. For BePO–X, the final cycle of least-squares calculations converged to give residuals of R_p = 6.20% and R_{wp} = 8.17% (χ^2 = 1.96) for 67 variable parameters and 3495 observations. Final atomic positional parameters for BePO–X are listed in Table I, with selected bond distance/angle data in Table II. The final observed, calculated, and difference profiles are illustrated in Figure 1. For ZnPO–X, residuals of R_p = 7.23% and R_w = 9.25% (χ^2 = 6.29) for 45 variable parameters and 3002 observations were obtained. Final atomic positional parameters for ZnPO–X are listed in Table III, with selected bond distance/angle data in Table IV. The final observed, calculated, and difference profiles are illustrated in Figure 2.

Further evidence for the 1:1 Zn/Be:P ordering scheme comes from ^{31}P solid-state MAS NMR data.[11] Both BePO–X and ZnPO–X showed a single, sharp phosphorus resonance at –8.2 and +5.8 ppm, respectively, relative to H_3PO_4, indicating only one phosphorus environment in these phases, in accordance with a perfect 4:0 cation ordering scheme with no P–O–P links, and by implication,

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(11) NMR spectra were obtained on a General Electric GN-300 instrument using a multinuclear broadband MAS NMR probe from Doty Scientific (spinning speed = 3–5 kHz). Data were collected in single-pulse mode, with a 45° pulse length of 2 μs and recycle delay time of 1 min for ^{31}P and a 3-μs 45° pulse, 10-s recycle delay for ^{9}Be. Details will be published later.

Table III. Final Atomic Coordinates for ZnPO–X (Cubic, Space Group $F\bar{d}3$, a = 25.1991 (5) Å)

atom	x	y	z	occ^a	$100U_{iso}$
Zn(1)	–0.0510 (2)	0.1195 (2)	0.0416 (2)		2.5 (1)
P(1)	–0.0524 (3)	0.0312 (3)	0.1263 (3)		2.5 (1)
O(1)	–0.0975 (4)	–0.0059 (5)	0.1145 (5)		2.5 (1)
O(2)	–0.0037 (5)	0.0027 (5)	0.1527 (4)		2.5 (1)
O(3)	–0.0329 (5)	0.0557 (4)	0.0739 (4)		2.5 (1)
O(4)	–0.0738 (5)	0.0725 (5)	0.1654 (5)		2.5 (1)
Na(1)	0	0	0	1.0^b	1.2 (5)
Na(2)	0.2376 (5)	0.2376 (5)	0.2376 (5)	0.87 (3)	1.2 (5)
O$_w$(1)^c	0.241 (2)	0.957 (2)	0.659 (2)	0.24 (2)	4.0^b
O$_w$(2)^c	0.0253 (8)	0.006 (2)	0.6590 (9)	0.53 (2)	4.0^b
O$_w$(3)^c	0.0152 (9)	0.0152 (9)	0.7347 (9)	0.73 (4)	4.0^b

^{a} Fractional site occupancy. ^{b} Not refined. ^{c} Water molecule.

Table IV. Selected Bond Distance (angstroms) and Angle (degrees) Data for ZnPO–X

Zn(1)–O(1)	1.915 (8)	Zn(1)–)(2)	1.960 (8)
Zn(1)–O(3)	1.858 (8)	Zn(1)–O(4)	1.909 (8)
P(1)–O(1)	1.502 (8)	P(1)–O(2)	1.570 (8)
P(1)–O(3)	1.538 (7)	P(1)–O(4)	1.532 (8)
Na(1)–O(3)	2.475 (10) × 6	Na(2)–O(2)	2.19 (2) × 3
Na(2)–Ow(2)	2.81 (3) × 3	Na(2)–Ow(3)^a	1.2 (3)
Ow(1)–Ow(2)^a	2.13 (4)	Ow(2)–Ow(3)^a	1.94 (3)
O–Zn(1)–O^b	109 (2)	O–P(1)–O^b	109 (2)
Zn(1)–O–P(1)^c	133 (2)		

^{a} Apparent contact due to fractional site occupancies. ^{b} Tetrahedral average. ^{c} Bridging oxygen average.

NA/TMAOH–ZNPO–X   GIER
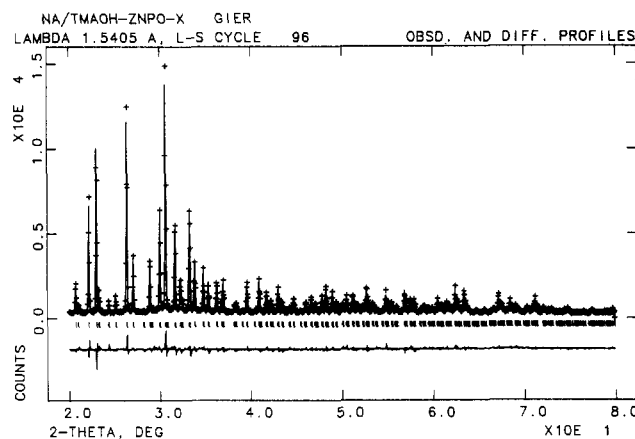LAMBDA 1.5405 A, L–S CYCLE   96   OBSD. AND DIFF. PROFILES

Figure 2. Final observed (crosses), calculated (line), and difference profile plots, with reflection positions indicated by tickmarks for ZnPO–X (X-ray data).

no M–O–M (M = Zn, Be) links in the structure. Additionally, ^{9}Be MAS NMR of BePO–X shows a sharp singlet (line width = 19 Hz) at –1.7 ppm relative to 1 M Be(NO$_3$)$_2$ (aq).

Thermogravimetric analysis data were collected on a Du Pont 9900 system. The hydrated BePO–X shows a weight loss in air of ca. 22%, corresponding almost exactly to an irreversible transformation from NaBePO$_4$·2H$_2$O to NaBePO$_4$ (calculated weight loss = 22%), which is complete by 350 °C. Atomic analyses were performed by Galbraith Laboratories, Nashville, TN. Anal. found for BePO–X: Na, 15.0; Be, 5.5; P, 18.3. Calcd: Na, 14.1; Be, 5.5; P, 19.0, assuming a stoichiometry of NaBePO$_4$·2H$_2$O. X-ray diffraction data show that the framework of BePO–X is stable to dehydration under vacuum at 150 °C and can be reversibly hydrated. Preliminary ion-exchange reactions carried out with BePO–X suggest that sodium is readily and completely exchangeable by silver, ammonium, cadmium, and copper.

Anal found for ZnPO–X: Zn, 32.2; P, 13.5; C, 2.83; N, 0.83; H, 3.30; Na, 7.31; water loss at 400 °C = 14.9–18%.

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This corresponds closely to the formula quoted above (calcd: Zn, 32.1; P, 14.0; C, 2.83; N, 0.83; H, 2.76; Na, 7.31; H_2O, 16.3). We believe this particular preparation contains a small amount of extraframework zinc. Of note is the Na:Zn ratio of 0.65, close to the crucial ratio of 0.67 in the synthesis.[8] X-ray data for ZnPO–X show that calcination at 250 °C destroys the framework, resulting in an amorphous product. The framework is less stable to exchange than that of BePO–X; exchange with Ca^{2+} proceeds normally, but Li^+ and Mg^{2+} convert the framework smoothly to other phases, while treatment with aqueous ammonium nitrate at room temperature results in the condensed "stuffed" tridymite-type phase NH_4ZnPO_4. After standing for 6 months in a closed container, hopeite ($Zn_3(PO_4)_2 \cdot 4H_2O$) lines appear in the X-ray powder diffraction pattern.

These new ZnPO–X and BePO–X phases crystallize in the faujasite-type zeolite X structure, which consists of cuboctahedral sodalite or β-cages,[3,10] linked via double 6-rings or hexagonal prisms in a diamond-like array. The framework surrounds large "supercages", which correspond to about 50% "empty space" in volume percentage, as described previously.[3] The framework consists of 1 Zn/Be atom and 1 P and 4 O atom sites, all on general crystallographic positions. The framework atoms' unit cell content is $(Zn/Be)_{96}P_{96}O_{384}{}^{96-}$, with charge compensation provided by the extraframework species: for BePO–X sodium cations, and for ZnPO–X, sodium, tetramethylammonium, and possibly zinc cations.

For BePO–X, the framework-atom geometry is in good accordance with the expected behavior for these species (d_{av}(Be–O) = 1.61 (5) Å, d_{av}(P–O) = 1.55 (6) Å). The three distinct locations of the sodium cations, all on the body diagonal of the cubic cell, are similar to those found in studies of dehydrated sodium aluminosilicate-X phases.[12] The first, at the origin (S_I site in standard notation),[10,12] approximately octahedrally coordinated by O(3) (d(Na-(1)–O(3)) = 2.372 (8) Å), is located in the center of the hexagonal prism joining adjacent β-cages and is fully occupied (refined occupancy = 1.08 (7)). The $S_{I'}$ site (outside

face of the hexagonal prism; d(Na(2)–O(3)) = 2.22 (3) Å) appears to be occupied by Na^+, coordinated to three O(3)'s in pyramidal coordination (occupation factor = 0.47 (4)). A rather short Na(1)–Na(2) contact (2.72 (5) Å) results. Third, the S_{II} position ("free" 6-ring joining the β- and supercages), is fully occupied (occupation factor = 1.04 (7)), with three Na(3)–O(2) bond lengths of 2.28 (2) Å, again in pyramidal configuration. The total unit-cell occupancy of these three sites is ca. 63, leaving 33 sodium atoms unaccounted for. No other significant site populations were established from Fourier maps, suggesting that the other sodiums may be dispersed over a number of sites in the supercage.

The ZnPO–X framework atoms display their expected structural behavior, although restraints were required to ensure a stable refinement. The location of the sodium cations in ZnPO–X are similar to some of the positions found for Na^+ in samples of hydrated zeolite-X, although occupation factors from the present refinement should be regarded as provisional, as these sites are partially occupied by zinc. As for BePO–X, the S_I and S_{II} sites are occupied by sodium, with occupancies of 1.0 and 0.87 (3), respectively. The S_I site shows octahedral oxygen coordination (d(Na(1)–O(3)) = 2.475 (10) Å), and the S_{II} site 3-fold sodium–oxygen geometry (d(Na(2)–O(2) = 2.190 (11) Å). Conversely, *no* significant population was detected for the $S_{I'}$ position, inside the sodalite β-cage. Conceivably, the TMA^+ cation occupies the β-cage and plays a significant templating role during the formation of the framework. The total unit-cell occupancy of the two sodium sites is 44, requiring a charge of +52 to be made up by the other extraframework species.

These new ZnPO–X and BePO–X phases are representatives of an extensive new class of zeolite materials not based on group IIIa or group IVa metal atom framework compositions. The zinc phosphate/arsenates[8] are the first examples of zeolite structural analogues containing only group IIb metals. Further work on the preparation, modification, and characterization of these and related systems is in progress.

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