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$Na_3H_x(H_2PO_4)_x[(GeO)_4(GeO_4)_3]\cdot 4H_2O$: A Rhombohedrally-Distorted Germanium Pharmacosiderite Analog with Anion/Cation Exchange Capabilities

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A rhombohedrally distorted germanium pharmacosiderite analog, with the stoichiometry of $Na_3H_x(H_2PO_4)_x[(GeO)_4(GeO_4)_3]\cdot 4H_2O$, $x \approx 1.38$, has been synthesized under mild conditions. As synthesized, this material contains both sodium cations and hydrogen phosphate anions as included species. Both monovalent/divalent cations and a variety of anions are easily exchanged in and out of the framework under aqueous conditions at room temperature. Depending on the ions incorporated, the crystal structure can be transformed to the cubic system [space group $P\bar{4}3m$ (No. 215)] and then back to the rhombohedral system. It appears that the incorporation of a sodium cation and *any* anion will induce the rhombohedral distortion. Rietveld refinement of room-temperature powder X-ray and low-temperature time-of-flight neutron powder data confirmed the space group $R3m$ (No. 160) with $a = 7.7121$ (4) Å and $\alpha = 89.04$ (3)°, final $R = 3.32\%$ and $R_w = 3.93\%$ ($\chi^2 = 5.055$) for 63 variables and 10 693 observations. Crystallographic data for two ion-exchanged cubic frameworks are included along with data for a synthetic cubic $K_3H[(GeO)_4(GeO_4)_3]\cdot 4H_2O$ [K/Ge] framework. Further analytical studies, such as ^{31}P MAS NMR and FTIR, were used to confirm the presence or absence of cation and/or anion exchange for all analogs studied.

Introduction

Non-aluminosilicate molecular sieves are of great interest because of their possibilities as catalysts, sorbents, and sensors.[1] Many of these new materials form frameworks that are isostructural with the aluminosilicates and also follow a strict alternation of tetrahedral atoms (T atoms) in the framework, yet in general have greatly varying molecular sieving properties and thermal stabilities. However, one common trait among the separate systems is that they are cation exchangers.

Pharmacosiderites are molecular sieves built from MO_6/XO_4 units and found to occur naturally as iron arsenates, with the framework formula $[Fe_4(OH)_4(AsO_4)_3]^-$ and charge balanced by potassium cations.[2,3] This framework encloses eight-membered rings with a three-dimensional network of pores, with intercage openings of approximately 4.3 Å. Previous studies have indicated that the vast majority of pharmacosiderite analogs retain the cubic space group $P\bar{4}3m$ (No. 215) upon ion exchange with various alkali-metal hydroxides. The possible distortions to body-centered cubic cells and a tetragonal cell were similarly reported, though crystal structures were not determined.[4] There are also reports of aluminoarsenate pharmacosiderite analogs, which retain their cubic space even upon ion exchange.[5,6] These frameworks have been extensively characterized by NMR, adsorption measurements, thermal studies, and recently with ionic conductivity studies.[7-9] However, less work has been done on structure analysis through X-ray diffraction methods. There has been an increased interest in the microporous germanate systems, in particular the germanium analog of pharmacosiderite and its various ion-exchanged analogs. This framework is similar to the mineral form; however, it consists of GeO_4 tetrahedra which corner share edge- and face-sharing GeO_6 octahedra. Of the various systems studied, including NH_4^+, Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Tl^+, Pb^{2+}, and Ba^{2+} included ions, framework substitution with phosphorus for germanium, and various amounts of extra framework water and/or molecules, none distorted from cubic symmetry and there is no evidence of anion exchange.[10-17] No cations positions were determined in these studies.

In this paper we report the synthesis and characterization of a rhombohedrally distorted germanium pharmacosiderite analog, $Na_3H_x(H_2PO_4)_x[(GeO)_4(GeO_4)_3]\cdot 4H_2O$ [Na/P/Ge], that has the unique ability to exchange *both*

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cations and anions from its cage, and incorporate a large number of monovalent/divalent cations and anions.

Furthermore, analytical experiments show that the presence of *both* the sodium cation and an anion is the cause of the rhombohedral distortion. Cation siting has been determined for the first time for the cubic phases Cs/Na/Ge, Ca/Li/Ge, and K/Ge.

Experimental Section

Na/P/Ge was conveniently synthesized as a microcrystalline white powder by preparing a solution of 1.197 g (4 mmol) of 4 M H_3PO_4, 3.63 g (36 mmol) of tetraethylamine, 5.09 g (280 mmol) of H_2O, and 0.163 g (4 mmol) of 49% HF in a polypropylene bottle. The addition of 3.10 g (4 mmol) of 1 M Na_6GeO_4 solution yielded a white milky slurry. This slurry was heated at 100 °C for 3 days (or 70 °C for 4–5 days), after which 0.5 g of product was recovered by vacuum filtration. The product was suitable for structure determination.

Simple substitution of D_2O for H_2O into the Na_6GeO_4 solution and vacuum filtration under flowing N_2 yielded the same product, yet then suitable for pulsed neutron diffraction studies.

Ion exchange involved the exchange reaction of the material twice in aqueous 10% salt (10 mL/g) at room temperature for 1.5 h. The resulting powder was vacuum filtered and washed thoroughly with deionized water. The salts included in analysis were monovalent and divalent cations and various nitrates, phosphates, and carbonates: $CsNO_3$, $LiNO_3$, Na_2HPO_4, KNO_3, $NaNO_3$, $Ca(NO_3)_2$, $Ba(NO_3)_2$, and Cs_2CO_3.

The cubic K/Ge analog was similarly synthesized as a microcrystalline white powder by having prepared the same starting solution of 4 M H_3PO_4, tetraethylamine, H_2O, and HF in a polypropylene bottle. The addition of 3.10 g (4 mmol) of 1 M K_4GeO_4 solution yielded a white milky slurry. This slurry was heated at 100 °C for 3 days (or 70 °C for 4–5 days), after which 0.6 g of product was recovered by vacuum filtration. The product was suitable for structure determination by powder methods.

Analytical Data. High-resolution X-ray diffraction data were collected at room temperature (25 (1) °C) on a Scintag PAD-X automated diffractometer, with θ–θ sample geometry and Cu Kα radiation, between 2θ = 18 and 100° in 0.02 steps for a total of 4099 data. The instrumental Kα_1/Kα_2 profile was reduced to a single Cu Kα_1 peak position (λ = 1.541 78 Å) by a stripping routine, and *d* spacings were established using silicon powder (a = 5.430 35 Å) as an internal standard, relative to this wavelength.

The intense pulsed neutron source (IPNS) at Argonne National Laboratories was used to collect time-of-flight diffraction data on 8 g of the polycrystalline sample. Data were collected for 10 h both at room temperature and ambient pressure and then at 25 K. The data sets were at 2θ angles of ±148°, ±90°, and ±60° over a cumulative *d*-spacing range of approximately 0.479–2.970 Å. Rietveld refinements were carried out using the program GSAS.[18]

^{31}P MAS NMR data were collected on a General Electric GN-300 spectrometer system, at 121.65 MHz (field strength 7.05 T). A multinuclear broad band was used in single-pulsed mode, with a 45° pulse length of 3 μs and recycle delay time of 5 min, referenced to 85% H_3PO_4.

FTIR spectra were obtained on a Digilab FTS-60 FTIR spectrometer with a pressed KBr pellet of sample.

Thermogravimetric analysis (TGA) data were collected on a duPont 9900 system. Samples were heated at 10 °C/min under flowing N_2 gas.

Elemental analysis was performed for two samples, the rhombohedrally distorted Na/P/Ge phase and the induced cubic Cs/Na/Ge phase (Galbraith Laboratories, Knoxville, TN).

Results. *Na/P/Ge*: The Na/P/Ge distorted pharmacosiderite was rhombohedral, a = 7.72 Å and α = 89.5°, as determined by room-temperature X-ray diffraction, with further X-ray studies used to determine the space group as $R3m$ (see below). Elemental analysis (Na, 9.19%; P, 0.46%. Calcd Na, 6.7%; P, 0.47%) showed that both phosphorus and sodium were present in the sample and indicate a stoichiometry of approximately $Na_3H_x(H_2PO_4)_x[(GeO_4)_3(GeO)_4]\cdot 4H_2O$, with $x \approx 1.38$. ^{31}P MAS NMR spectroscopy revealed one major peak at 4.2 ppm, assigned to Na_2HPO_4, and three minor peaks at 11.28, −3.25, and −12.95 ppm, assigned to various sodium phosphate chemical shifts, after 120 scans and a spinning speed of approximately 6.2 kHz (see Figures 8). For comparison with ion-exchanged materials (see below), FTIR data were collected on the sample. As was expected, there was no peak in the region of a nitrate stretching band.

$LiNO_3$ exchange: The Na/P/Ge distorted pharmacosiderite was ion exchangeable with Li^+ cations. The Li/P/Ge cubic pharmacosiderite was prepared by ion exchange with $LiNO_3$ (10 mL/g). The resulting powder was filtered and washed thoroughly with water. The material was cubic, a = 7.708 (2) Å, as determined by room-temperature X-ray diffraction, with space group $P\bar{4}3m$. ^{31}P MAS NMR spectroscopy revealed two small peaks at −3.25, and −12.953 ppm, after 81 scans and spinning speed of approximately 5.4 kHz. Because these small peaks were matched exactly with the small shifts in the Na/P/Ge (separate from the strongest peak at 4 ppm), we believe that there was some small amount of phosphorus remaining in the cage. FTIR data of the ion-exchanged product contained a strong sharp peak at 1387 cm^{-1}, in the region of a nitrate stretching band, and indicative of newly included nitrate anions in the framework. The FTIR and NMR data showed that most of the phosphate anions had been exchanged by nitrate anions in the cage.

$CsNO_3$ exchange: The Na/P/Ge distorted pharmacosiderite was ion exchanged with $CsNO_3$ to produce the Cs/Na/Ge analog. The resulting powder was filtered and washed thoroughly with water. The material was cubic, space group $P\bar{4}3m$, a = 7.723 (6) Å, as determined by room-temperature X-ray diffraction (see Table 2 of the supplementary material). Elemental analysis (Cs, 13.19%; Na, 4.43%, P, 0.20%. Calcd Cs, 12.7%; Na, 4.4%; P, 0.2%) showed that cesium had exchanged into while phosphorus had exchanged out, of the sample, whose stoichiometry is approximately $CsNa_2H_{2x}(NO_3)_x(H_2PO_4)_x[(GeO)_4(GeO_4)_3]\cdot 4H_2O$, with $x \approx 1.38$. The ^{31}P MAS NMR data of 77 acquisitions and a spinning speed of approximately 5.6 kHz revealed no observable peak. FTIR contained a weak yet sharp nitrate stretching band at 1389 cm^{-1}, implying that the nitrate anion has been primarily exchanged for the phosphate anion in the cage.

$Ca(NO_3)_2$ exchange: The Na/P/Ge distorted pharmacosiderite was ion exchanged with $Ca(NO_3)_2$ to produce the Ca/Na/Ge analog. The resulting powder was filtered and washed thoroughly with water. The material was rhombohedral, space group $R3m$, a = 7.725 (2) Å and α = 89.3 (4)°, as determined by room-temperature X-ray diffraction (see Table 3 of the supplementary material) The ^{31}P MAS NMR with 126 acquisitions and a spinning speed of approximately 5 kHz had one small peak, seen at 3.164 ppm. FTIR data contained a medium-strength sharp peak at 1389 cm^{-1}. The observance of a $-NO_3$ stretching band and a weak phosphorus NMR chemical shift indicated there are a mixture of anions in the cage. On the basis of the Cs/Na/Ge data, some sodium is assumed to remain in the framework cage.

$Ba(NO_3)_2$ exchange: The Na/P/Ge distorted pharmacosiderite was ion exchanged with $Ba(NO_3)_2$ to produce the Ba/Ge analog. The resulting power was filtered and washed thoroughly with water. The material was rhombohedral, space group is $R3m$, a = 7.68 (3) Å and α = 89.73 (3)°, as determined by room-temperature X-ray diffraction. The ^{31}P MAS NMR with 80 acquisitions and a spinning speed of approximately 5.2 kHz had no peaks. FTIR data contained a weak yet sharp peak at 1384 cm^{-1}, indicating predominant nitrate presence with the framework. The observance of a $-NO_3$ stretching band and no phosphorus NMR peaks implied there are mainly nitrate anions exchanged into the cage.

Na_2HPO_4 exchange of cubic Li/P/Ge: The material was rhombohedral with space group $R3m$ with a = 7.745 (2) Å and α = 89.08 (4)°, as determined by room-temperature X-ray diffraction. The ^{31}P MAS NMR with 107 scans and a spinning speed of approximately 5.4 kHz had one small peak at −10.727 ppm. FTIR data contained a very small yet sharp nitrate stretching band at 1384 cm^{-1}. The observance of a $-NO_3$

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[18] Larson, A. C.; Von Dreele, R. B. *GSAS User Guide*; Los Alamos National Laboratory; Los Alamos, NM 87545, 1985–1988.

stretching band and a weak NMR chemical shift implied that some of the nitrate anions were exchanged for phosphate anions in the cage.

$NaNO_3$ exchange of cubic Li/P/Ge: The room-temperature exchange resulted in a rhombohedrally distorted cell (Na/Li/Ge), space group $R3m$, with a = 7.725 (3) Å and α = 89.3 (4)°. The ^{31}P MAS NMR with 140 acquisitions and a spinning speed of approximately 6 kHz showed no observable peak. FTIR data contained a weak yet sharp nitrate stretching band at 1390 cm^{-1}. The observance of a $-NO_3$ stretching band implied the nitrate anions exchanged in the cage.

K_2HPO_4 exchange of cubic Li/P/Ge: The room-temperature exchange resulted in a cubic cell (K/Li/Ge), space group $P\bar{4}3m$, with a = 7.6633 (9) Å. The ^{31}P MAS NMR with 72 acquisitions and a spinning speed of approximately 5.3 kHz showed no observable peak. The FTIR data contained a sharp nitrate stretching band at 1380 cm^{-1}. The observance of a weak $-NO_3$ stretching band implied nitrate anions remained in the cage.

$Ca(NO_3)_2$ exchange of cubic Li/P/Ge: The room-temperature exchange resulted in a cubic cell (Ca/Li/Ge), space group $P\bar{4}3m$, with a = 7.696 (2) Å. The ^{31}P MAS NMR with 117 acquisitions and a spinning speed of approximately 5 kHz showed no observable peak. The FTIR data contained a sharp nitrate stretching band at 1389 cm^{-1}. The observance of a $-NO_3$ stretching band and the absence of a phosphorus NMR peak implied nitrate anions remained in the cage. The powder X-ray diffraction data were refined (see below), with a resulting approximate stoichiometry of $CaLiH_{2x}(NO_3)_x(H_2PO_4)_x[(GeO)_4(GeO_4)_3]\cdot 4H_2O$, with $x \approx 1.38$.

Cs_2CO_3 exchange of distorted Na/P/Ge: The room-temperature exchange resulted in a cubic cell ($Cs/CO_3/Ge$), space group $P\bar{4}3m$, with a = 7.753 (2) Å. The ^{31}P MAS NMR with 80 acquisitions and a spinning speed of approximately 5 kHz showed no observable peak. The FTIR data contain a peak at 1383 cm^{-1}, which could be assigned to the $-(CO_3)^{2-}$ stretching band. The observance of a FTIR band and an increased cubic cell implied the carbonate anion exchanged into the cage for most of the phosphate anions in the cage.

Cubic K/Ge: The room-temperature synthesis with potassium as the charge-balancing cation resulted in a cubic cell (K/Ge), space group $P\bar{4}3m$, with a = 7.677 (3) Å. The ^{31}P MAS NMR with 64 acquisitions and a spinning speed of approximately 5 kHz showed no observable peak. The FTIR data contained no stretching peaks in the area of the nitrate anion. These analytical data suggested that there was no anion present in this cubic cell.

Structure Determination

Rietveld refinements of four representative powders were performed in this study: the rhombohedrally distorted Na/P/Ge, the cubic Cs/Na/Ge, the cubic Ca/Li/Ge, and an "as-synthesized" (non-phosphorus containing) K/Ge cubic phase.

Na/P/Ge. A room-temperature powder X-ray diffraction pattern was indexed, based on a rhombohedral unit cell, with lattice constants of approximately a = 7.7 Å and $\alpha \approx 90°$. The material had a similar peak profile to a cubic $K_3H[(GeO)_4(GeO_4)_3]$ (space group $P\bar{4}3m$) pharmacosiderite, yet with no systematic absences indicating $R3m$ as a possible space group. Furthermore, information combined from X-ray diffraction, elemental analysis and TGA (6.7% weight loss) data indicated $Na_3H_x(H_2PO_4)_x[(GeO_4)_3(GeO)_4]\cdot 4H_2O$, with $x \approx 1.38$, as the model stoichiometry.

The structure was solved by lowering of symmetry of the atomic general positions of the framework elements and extraframework water oxygen atoms of the iron arsenate mineral pharmacosiderite in the cubic group $P\bar{4}3m$ (No. 215) to similar atomic general positions in space group $R3m$ (No. 160), while maintaining the multiplicities of each site. To describe the process used, the pharmacosiderite formula is generically written as $A_3M_4O_4X_3O'_{12}$. For the octahedral element M with the position (x,x,x), the new positions are M_1 at (x,x,x) multiplicity = 1 and M_2 at (x,x,z) multiplicity = 3. For the tetrahedral element X with position $(^1/_2,0,0)$, the new position is X at (z,x,x) with multiplicity = 3. For oxygen = O_1 (x,x,x), the new positions are O_1 at (x,x,x) multiplicity = 1 and O_2 at (x,x,z) with multiplicity = 3. For the oxygen atoms O′ at (x,x,z), there are two oxygen atoms at (x,x,z) (O_1' and O_2') each with multiplicity = 3 and O_3' at (x,y,z) with multiplicity = 6 (see Table 1 of the supplementary material).

The Rietveld profile refinement began with the manual altering of the α value off 90°, while retaining the unit cell length, and lattice constant determination with the POWPREF option of GSAS.[18] The framework atomic coordinates were determined by the new lower symmetry space group and entered accordingly. After the usual refinement of scale factor, detector zero-point correction, background coefficients, unit-cell parameter, peak shape-width variation terms, and framework-atom positional and isotropic thermal parameters, the profile R factor was over 20%.

Some of the extraframework atom positions were determined by repeated difference Fourier syntheses and were assumed to be oxygen atoms of water molecules. One oxygen atom was located at a (xxx) special position, two were found at different (zxx) special positions, and a final oxygen atom was found at a (xxz) special position. Refinement lowered the profile R factor to 11.5%. The remaining ions (Na^+, HPO_4^{2-}) were known to be present from elemental analysis but could not be unambiguously located by Fourier difference maps and are believed to reside inside the cage of this molecular sieve, disordered over the water oxygen atom sites (whose fractional occupancies ≤1.0). The best convergence value was ensured by careful thermal constraints and positional refinements of all atoms. The final cycle of least-squares calculations converged to give residuals of R = 5.95%, R_w = 8.44% (χ^2 = 3.528) for 42 variables and 4099 observations (see Table 2 of the supplementary material).

In an effort to distinguish between the intercage ions, a deuterated sample was prepared, as described earlier, and 15 K time-of-flight neutron powder diffraction data were collected. The Rietveld profile refinement was performed using GSAS. Refinement began with the cell and atomic parameters determined by X-ray refinement. After the refinement of scale factor, detector zero-point correction, beckground coefficients, unit-cell parameter, peak shape-width variation terms, and both framework and intercage water oxygen-atom positional and isotropic thermal parameters, the profile R factor was approximately 4%. Repeated Fourier difference syntheses found no other sites in the cage. This supports the original belief that both the cations and the anions in the cage are disordered over the water–oxygen atom sites. The final residuals were R = 3.32% and R_w = 3.93% (χ^2 = 5.055) for 63 variables and 10 693 observations (see Table 2 of the supplementary material). The final observed, calculated, and difference X-ray profiles are illustrated in Figure 1.

Cs/Na/Ge. The crystal structure of this cubic (space group $P\bar{4}3m$) material was established by X-ray Rietveld refinement, using the starting potassium and cesium iron arsenate models of pharmacosiderite in space group $P\bar{4}3m$.[2,3] Elemental analysis and TGA (6.8% weight loss) indicated a model stoichiometry of $CsNa_2H_{2x}(NO_3)_x(H_2PO_4)_x[(GeO_4)_3(GeO)_4]\cdot 4H_2O$, $x \approx 1.38$. Refinement was

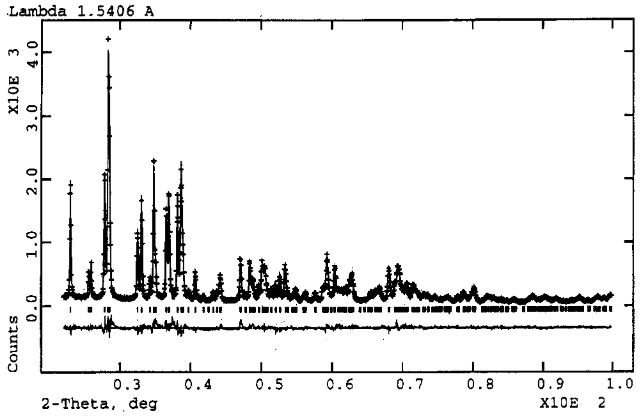

Figure 1. Final observed, calculated, and difference profiles of Na/P/Ge room-temperature powder X-ray diffraction data.

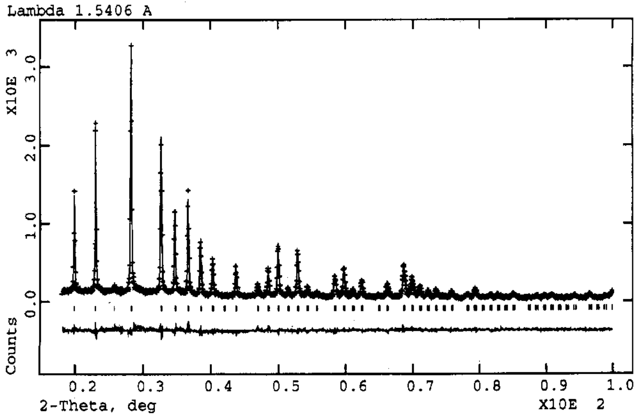

Figure 2. Final observed, calculated, and difference profiles of Cs/Na/Ge room-temperature powder X-ray diffraction data.

carried out on X-ray powder diffraction data collected at room temperature. With the Cs/Na/Ge, the profile *R* factor was 10.19% with 17 variables refining (including framework atoms and included water oxygen atoms) but without a cation in the cage. The cation position was known to be close to ($^1/_2$,$^1/_2$,0), but no literature refinement was reported.[3] Elemental analysis indicated that the cations present were cesium and sodium. Inputting the heavier cation, Cs^+, close to this site yet off the zero coordinate, allowed for a best convergence of least-squares cycles. The final refined position was ($^1/_2$,$^1/_2$,0.055). The final residuals were $R = 8.54\%$ and $R_w = 11.3\%$ ($\chi^2 = 1.859$) for 26 variables and 4099 observations (see Table 3 of the supplementary material). The final observed, calculated and difference profiles are illustrated in Figure 2.

Ca/Li/Ge. Refinement in cubic space group $P\bar{4}3m$ was carried out on X-ray powder diffraction data collected at room temperature. With the Ca/Li/Ge, the profile *R* factor was 12% with 17 variables refining, but without a cation in the cage. Inputting the Ca^{2+} close to the ($^1/_2$,$^1/_2$,0.092) site allowed for a good convergence of least-squares cycles. However, the values further improved with the addition of Li^+ disordered on that site (known to be included from elemental analysis). The final residuals were $R = 6.67\%$ and $R_w = 8.63\%$ ($\chi^2 = 2.737$) for 23 variables and 4099 observations. The final formula was approximated to $CaLiH_{2x}(NO_3)_x(H_2PO_4)_x[(GeO)_4(GeO_4)_3]\cdot 4H_2O$, with $x \approx 1.38$ (see Table 4 of the supplemental material). The final observed, calculated and difference profiles are illustrated in Figure 3.

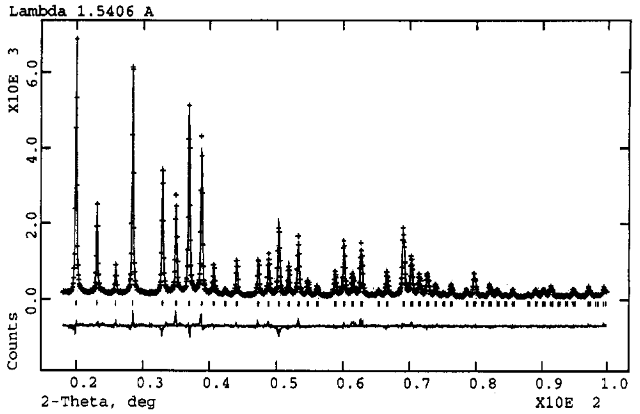

Figure 3. Final observed, calculated, and difference profiles of Ca/Li/Ge room-temperature powder X-ray diffraction data.

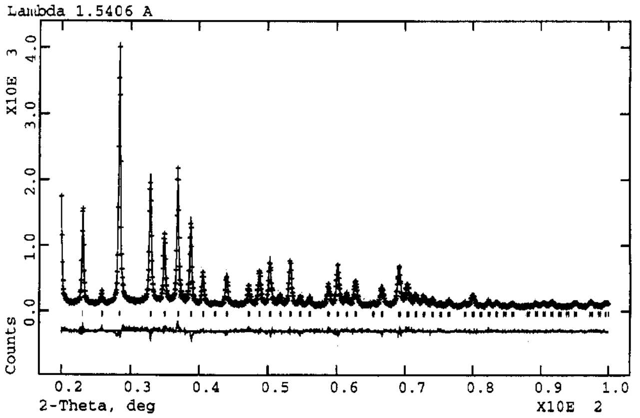

Figure 4. Final observed, calculated, and difference profiles of K/Ge room-temperature powder X-ray diffraction data.

K/Ge. Refinement on the "as-synthesized" cubic material ($a = 7.6763$ (3) Å), with space group $P\bar{4}3m$, was carried out on X-ray powder diffraction data collected at room temperature. With the K/Ge, the profile *R* factor was 11.6% with 17 variables refining, including intercage water oxygen atom positions and thermal factors, but without the cation in the cage. Inputting the K^+ close to the ($^1/_2$,$^1/_2$,0.05) site allowed for the best convergence of least-squares cycles. Repeated Fourier syntheses revealed no other sites occupied in the cage. The final residuals were $R = 6.90\%$ and $R_w = 9.16\%$ ($\chi^2 = 1.827$) for 23 variables and 3999 observations, for the molecular formula $K_3H[(GeO)_4(GeO_4)_3]\cdot 4H_2O$. The refinement shows that even under the same reaction conditions and using the same reactants, if the sodium cation is not present, the rhombohedrally distorted cell will not be formed (see Table 5 of the supplementary material). The final observed, calculated, and difference profiles are illustrated in Figure 4.

The stoichiometry for only four members of the series have been calculated through the combination of crystallographic refinements, elemental analyses, and MAS NMR. Due to the very small scattering factor of lithium resulting in near invisibility to X-rays, those compounds exchanged with it were assumed to have complete exchange of the Li^+ for Na^+. We assume that the remaining series members follow the same pattern of partial ion exchange.

Discussion

Various analytical results provided evidence for the reversible distortion of the rhombohedral cell to a cubic

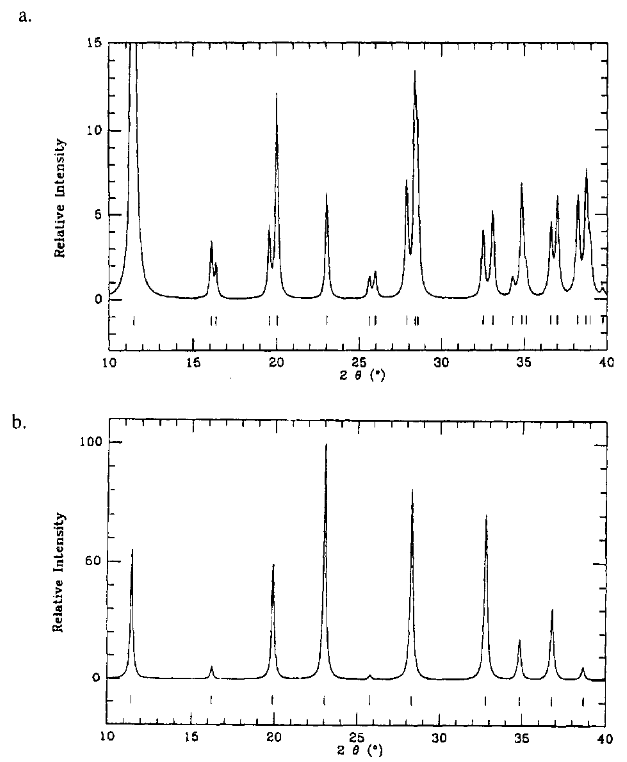

Figure 5. LAZY-PULVERIX[19] powder X-ray diffraction pattern simulation of (a) the rhombohedral Na/P/Ge and (b) the cubic Cs/Li/Ge.

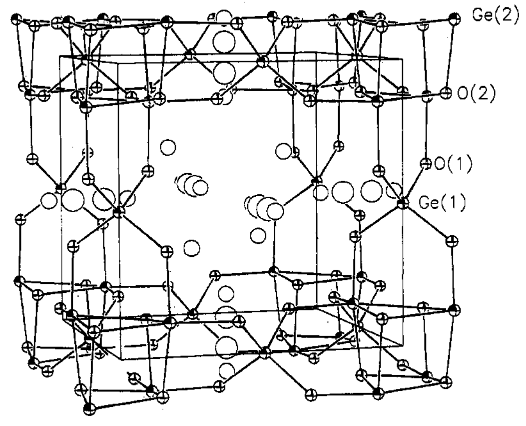

Figure 6. ORTEP[20] diagram of the cubic Cs/Li/Ge unit cell.

cell upon ion exchange. Crystallographically, we have seen that the rhombohedral cell has a similar X-ray powder pattern to the cubic cell.

Inspection of the model unit cell from powder refinements, though, does not readily provide a clear view of the difference between the two frameworks. However, X-ray diffraction pattern simulations of both cages duplicate the observed data[19] (see Figure 5). Obvious differences are evident when the location of the intercage species are examined. In the case of the cubic phase, the cations (in this case Cs^+) and water molecules are ordered on their special positions (see Figure 6). However, Figure 7 of the distorted phase shows that not only are the sites for the ionic species not on high-symmetry positions, but also they are actually disordered over all sites (see Figures 6 and 7).

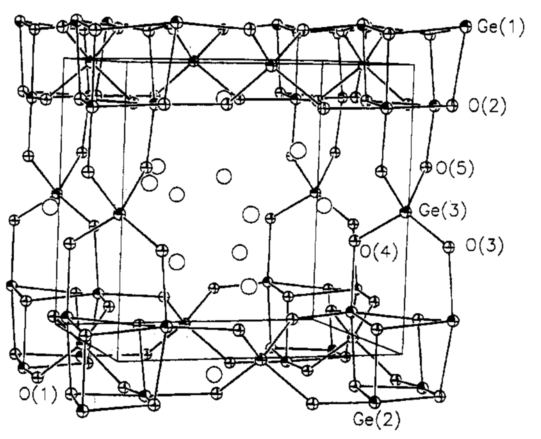

Figure 7. ORTEP[20] diagram of the rhombohedrally distorted Na/P/Ge unit cell.

When the refined crystallographic X-ray data are closely examined, both for the distorted cell and also in comparison to the cubic cells, interesting structural information is obtained. In the distorted Na/P/Ge framework, there are three crystallographically distinct germanium atoms; Ge(1) and Ge(2) are octahedrally bound to oxygen atoms, while Ge(3) is tetrahedrally bound to oxygen atoms (see Table 7 of the supplementary material). The wide range, yet within expected values, of bonds lengths is due to the type of Ge–O–Ge connectivity involved and also the distortion of the unit cell angles. Ge(1) and Ge(2) are tightly bound in a cubic substructure that is located at each of the corners of the unit cell. Half of their bonds are through oxygen atoms in the cube to the other octahedral germanium atom forming shorter bonds and near octahedron angles [d_{ave}(Ge–O) = 1.94 (2) Å, θ_{ave}(Ge–O–Ge) = 97.5 (5)°]. The other half of the octahedral Ge–O bonds are bound through the oxygen atom to the tetrahedrally bound germanium atom (Ge(3)). These bonds are much longer and the angles are approaching tetrahedral angles [$d_{\text{ave}}(\text{Ge–O})_{\text{oct}}$ = 2.0501 (4) Å, $\theta_{\text{ave}}(\text{Ge–O–Ge})_{\text{oct}}$ = 126.4 (2)°]. These are distinctly different from the totally tetrahedrally bound Ge(3) atoms. This atom is bound to only four oxygen atoms but has two short and two long bonds. If the cell did not have the rhombohedral distortion of the angles, these bond lengths and bond angles would be much closer in value. However, due to the distortion along the 3-fold axis, there is an asymmetry in bonding on the Ge(3) site, where bond angles decrease with O(5) while bond length increases according to Table 7 of the supplementary material. The sodium cation and the phosphate anion could not be located by either X-ray or neutron diffraction studies and are assumed to be disordered over the four water oxygen atom sites.

The induced cubic phases, whose structures were refined in space group $P\bar{4}3m$, show similar results to the rhombohedral cell. Using the cesium-exchange system as an example, there are now only two crystallographically distinct non-oxygen framework atoms, as in the previously studied minerals and synthesized pharmacosiderite analogs. The same cubic substructure is present in this framework, made of the octahedrally bound Ge(2) atom. It is bound to two different oxygen atoms with longer bonds (d_{ave}(Ge(2)–O) = 1.896 (8) Å) and near 90° bond angles (θ_{ave}(O–Ge(2)–O) = 93.2 (2)°). The center of the edges of the framework unit cell are occupied by the tetrahedrally bound Ge(1) atom. It is bound to the oxygen atom through a short bond (1.721 (8) Å) and four near-tetrahedral bond angles (θ_{ave}(O–Ge(1)–O) = 109.95 (2)°). The cesium cation,

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(19) Yvon, K.; Jeitschko, W.; Parthe, E. *LAZY-PULVERIX User Guide*; University of Geneva, Switzerland, 1976.

(20) Johnson, C. K. *Oak Ridge National Laboratory Report ORNL-5138*; Oak Ridge, TN, 37830, 1976, with local modifications.

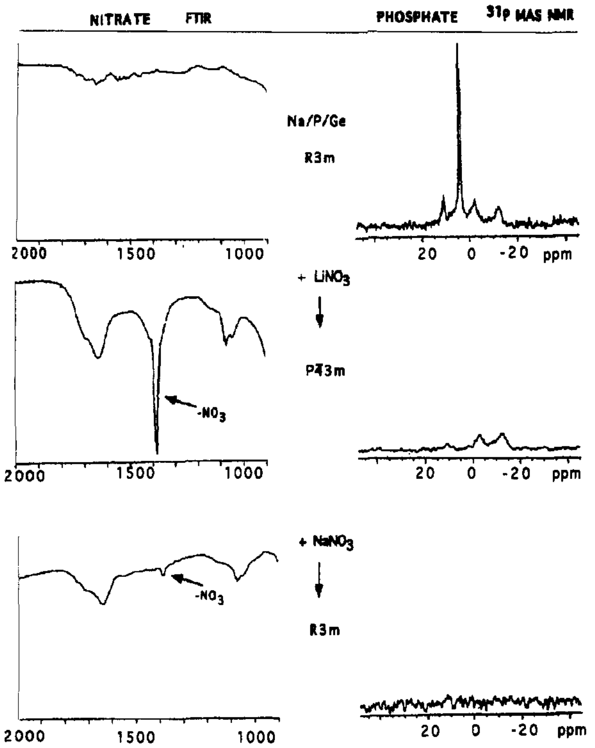

Figure 8. An example of the reversible rhombohedral distortion monitored by room-temperature powder X-ray diffraction, FTIR, and ^{31}P MAS NMR.

which may also have the nitrate anion disordered over the same site, is 8 coordinate to the framework oxygen atoms (d_{ave}(Cs–O(1)) = 3.205 (4) Å) and is also coordinated to the ordered, yet partially site occupied, water-molecule oxygen atoms included in the cage (see Table 11 of the supplementary material).

A sequence of experiments were performed that were designed to determine the cause of the distortion of a rhombohedral cell during synthesis and due to certain ion exchanges (see Figure 8). Starting with an "as-synthesized" distorted Na/P/Ge framework, the sample was ion exchanged with $LiNO_3$, under the previously mentioned conditions, to make the Li/P/Ge. The cell became cubic as determined by powder X-ray diffraction. The sample was analyzed by ^{31}P MAS NMR and shown to have only trace, disordered amounts of phosphate present in the cage. Furthermore, the FTIR spectra clearly showed the presence of a strong $-NO_3$ stretching band. Obviously most of the sodium cation and phosphate anion had been exchanged for the lithium cation and nitrate anion. The *same* sample was then further exchanged with $NaNO_3$ to make the Na/Ge system, under the before-mentioned conditions and was shown to redistort to the rhombohedral space group of *R*3*m*. The sample was again analyzed by the same analytical methods and shown to only have the nitrate anion and mainly the sodium cation present.

In conjunction with the data from the Na_2HPO_4 exchange, it seems evident that the presence of a sodium cation and *any* anion in the cage of these germanium pharmacosiderite analogs induces the rhombohedral distortion in the framework. It is significant to note that a distortion does not seem to be induced on the first-synthesized cubic systems that are widely known and studied, but a rhombohedral to cubic to rhombohedral distortion can be induced by ion exchange of the Na/P/Ge. Furthermore, the unique ability for this molecular sieve to exchange not only the cation but also the anion can be easily monitored by the methods employed in the experiment above.

Summary

We have synthesized and characterized a distorted rhombohedral germanium pharmacosiderite framework analog, which transforms reversibly to the cubic modifications upon ion exchange. With only one reference to a possible tetrahedrally distorted pharmacosiderite after ion exchange with Ba^{2+},[4] research has not uncovered this interesting molecular sieve until now. This framework is of interest not only because of its ease of synthesis and interesting crystallographic distortion but also because the included anion and cation from synthesis are reversibly exchangeable. There are a very small number of such molecular sieves known and well characterized to date. The characterization techniques, used to study many aspects of this molecular sieve and its ion-exchanged analogs, involved MAS NMR, FTIR, Rietveld refinement of powder X-ray and neutron diffraction data, and elemental analysis.

A complete picture of this class of sieve has been developed which shows that the rhombohedral distortion occurs due to the inclusion of both a sodium cation and an anion in the cage. The presence of both species occurs during the synthesis, thereby directly forming the rhombohedral crystal system. It is only after the material has been ion exchanged with either monovalent or divalent cations that the known cubic crystal system is observed. Further exchanges with sodium salts will reinduce the distortion; however the anion simply needs to be present to be rhombohedral. The included ion does not need to be phosphate to force the framework to distort off $\alpha = 90°$ and form in the rhombohedral structure. This theory is further supported when comparing as-synthesized cubic potassium germanium pharmacosiderite analog with the K/Li/Ge. This material (K/Ge) remains cubic after ion exchange and does not have an anion included in its cage as does the ion-exchanged K/Li/Ge framework (cubic, yet derived from the distorted cell and containing some phosphate anion).

Synthetic and characterization studies continue in order to further investigate the molecular sieving properties of this class of material, with leading interests lying in gas-separation applications suited to frameworks with pore opening of approximately 4.3 Å. However, further work is needed with these pharmacosiderite analogs in stabilizing the framework through dehydration.

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Supplementary Material Available: A listing of crystallographic and atomic positional parameters and thermal parameters for Na/P/Ge, Cs/Na/Ge, Ca/Li/Ge, and K/Ge (11 pages). Ordering information is given on any current masthead page.