Inorganic Chemistry

Communication

pubs.acs.org/IC

$K_4Fe_4P_5O_{20}$: A New Mixed Valence Microporous Compound with Elliptical Eight-Ring Channels

Zhangzhen He,*,[†] Weilong Zhang,[†] Wendan Cheng,[†] Atsushi Okazawa,[‡] and Norimichi Kojima[‡]

[†]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Mater, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

[‡]Graduate School of Arts and Sciences, University of Tokyo, Komaba 3-8-1, Meguro, Tokyo 153-8902, Japan

Supporting Information

ABSTRACT: A new small-pore compound $K_4Fe_4P_5O_{20}$ was obtained by conventional solid-state reaction in a closed crucible. The crystal structure is constructed by $Fe_4P_5O_{20}$ units forming chains along the *c* axis and elliptical eight-ring channels on the *a*−*b* plane in which K cations locate inside. Such structural characteristics seem to be quite similar to those seen in the natrolite family. However, Fe ions in $K_4Fe_4P_5O_{20}$ have trigonal−bipyramidal instead of common tetrahedral coordination. Furthermore, our experimental results combined from magnetic susceptibility and ^{57}Fe Mössbauer spectrum measurements show mixed valence Fe^{3+}/Fe^{2+} in the titled material. To the best of our knowledge, this is the first example that contains mixed valence iron ions in a so-called natrolite framework.

Zeolites are a class of microporous materials, which are widely used in practical applications such as catalysis, ion exchange, and gas separation. Generally, zeolites crystallize in a variety of low-density framework structures built by corner-connected networks of tetrahedral (TO_4), yielding cavities or channels of molecular dimensions. Traditionally, natural and synthetic zeolites are aluminosilicates with the numerous linkages of AlO_4 and SiO_4 tetrahedra that bound nanopores of various sizes. Among these aluminosilicate-based zeolites, natrolite ($Na_2Al_2Si_3O_{10}\cdot 2H_2O$) is one of the most interesting naturally occurring zeolites, for which the chemical composition was known in the early 1800s[1] and the crystal structure was established in 1930s.[2] The framework of natrolite is composed of $Al_2Si_3O_{10}$ units with SiO_4 and AlO_4 tetrahedra forming infinite chains along the *c* axis, and chains link each other to form a two-dimensional elliptical eight-ring channel on the *a*−*b* plane in which Na cations and water molecules locate inside (Figure 1a). Over the past several decades, such unique chemical and structural characteristics of natrolite have been extensively studied.[3−13] Since the discovery of a large family of aluminophosphate-based zeolites, the search for nonaluminosilicate-based microporous materials has become of considerable interest.[14] A large number of zeolites with new framework topologies based on gallogerminates,[15] aluminogerminates,[15] zincophosphates,[16] and aluminophosphates[17] have been synthesized using a substitution with tetrahedral GaO_4, GeO_4, ZnO_4, or PO_4 for AlO_4 or SiO_4, respectively. At present, about ∼190 natural and synthetic zeolite species with the opening sizes of pores and channels from 0.2 to 2 nm have been reported.[18]

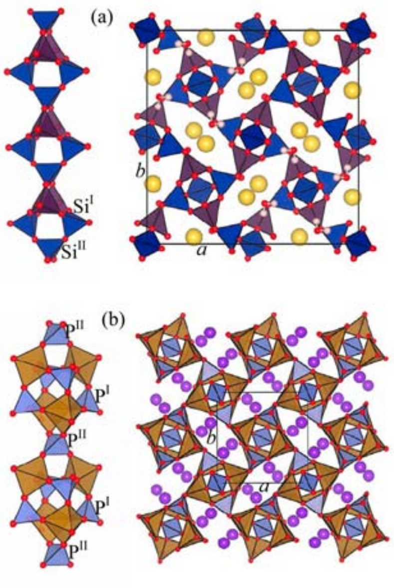

Figure 1. (a) The structure of natrolite $Na_2Al_2Si_3O_{10}\cdot 2H_2O$, where purple and blue tetrahedra represent AlO_4 and SiO_4, respectively; yellow, pink, and red balls are Na cations, H, and O atoms. (b) The structure of $K_4Fe_4P_4O_{20}$, where brown trigonal bipyramids, gray tetrahedra, and purple and red balls represent FeO_5, PO_4, K cations, and O atoms, respectively.

Because of the potential importance in industrial catalysis, many efforts have been made to obtain transition-metal-containing zeolite analogues.[19] An introduction of transition-metal cobalt into substituted aluminophosphates was successfully realized by controlling the ratio of Co/Al.[20] However, the percentage of transition-metal substitution is very limited in such Co−Al−P−O systems. In fact, a full (100%) substitution with transition-metal atoms for the tetrahedral-coordination of main group atoms (e.g., T = Si, Al, P, Ga, Ge, etc.) seems to be difficult, since the transition-metal atoms with large ion radii usually tend to form octahedral coordination in the oxygen-ligand environment according to the Pauling's rules.[21] Therefore, almost no zeolites, especially for natrolite-like materials

Received: June 12, 2012
Published: June 28, 2012

dx.doi.org/10.1021/ic301245c | *Inorg. Chem.* 2012, 51, 7469−7471

with transition metals (e.g., M = Ni, Co, Fe, Mn, etc.) in the framework built by (MO_n) and (TO_4) polyhedra, have been reported up to date.[22]

In this Communication, we report a new microporous compound $K_4Fe_4P_5O_{20}$. The framework is composed of FeO_5 and PO_4 polyhedra, forming elliptical eight-ring channels on the *a*−*b* plane which seem to be quite similar to those of $Na_2Al_2Si_3O_{10}\cdot 2H_2O$. However, $K_4Fe_4P_5O_{20}$ exhibits different oxygen-coordination and linkages of polyhedra, compared to $Na_2Al_2Si_3O_{10}\cdot 2H_2O$. Furthermore, the titled material is confirmed to have mixed valence Fe^{3+}/Fe^{2+} ions in the framework. To the best of our knowledge, $K_4Fe_4P_5O_{20}$ is the first ferrophosphate-based microporous material with a mixed valence.

Unlike almost all of the zeolite natrolite analogues synthesized with the hydrothermal method, single crystals of $K_4Fe_4P_5O_{20}$ were obtained by a conventional high-temperature solid-state reaction. The mixture of high purity reagents of K_2CO_3 (6.9 g), Fe_2O_3 (16 g), $NH_4H_2PO_4$ (23 g), and KF (5.8 g) was ground carefully to homogeneity in an agate mortar and then was fully packed into an alumina crucible (Φ42 × 50 mm^3). The crucible was capped with a cover using Al_2O_3 cement (C-989, Cotronics Corp.). Such a closed crucible was put into a homemade electric furnace, and then the furnace was heated up to 1050 °C and kept at 1050 °C for 10 h to ensure that the solution melted completely and homogeneously. The furnace was cooled slowly down to 700 °C at a rate of 1 °C/h, kept at a constant temperature, and then cooled down to room temperature at a rate of about 100 °C/h. With this procedure, gray crystals were obtained by mechanical separation from the crucible. It is noted that single crystals of $K_4Fe_4P_5O_{20}$ cannot be obtained successfully using K_2CO_3, Fe_2O_3, and $NH_4H_2PO_4$ as the starting materials under the same growth conditions owing to the large viscosity of the solution. To decrease the viscosity and to improve the crystallization, the mixtures of KF (5.8 g) and K_2CO_3 (6.9 g) were adopted instead of full K_2CO_3 (13.8 g) in this growth procedure. Also, the appearance of mixed valence iron ions (Fe^{3+}/Fe^{2+}) may be due to reducing gas NH_3 arising from the decomposition of $NH_4H_2PO_4$ in the closed crucible.

The crystal structure of $K_4Fe_4P_5O_{20}$ was solved and refined on the basis of the single-crystal data.[23] $K_4Fe_4P_5O_{20}$ crystallizes in the tetragonal system with space group $P\bar{4}2c$. As shown in Figure 1b, a three-dimensional (3D) framework is constructed from $Fe_4P_5O_{20}$ units which are composed of full corner sharing of FeO_5 trigonal bipyramids and PO_4 tetrahedra. The FeO_5 trigonal bipyramids are slightly distorted with different Fe−O distances (1.903−1.984 Å), while the PO_4 tetrahedra have two types of distorted P^IO_4 (P^I−O = 1.494−1.569 Å) and nondistorted $P^{II}O_4$ (P^{II}−O = 1.527 Å). FeO_5 trigonal bipyramids are linked with P^IO_4 tetrahedra to each other via a corner-sharing oxygen atom to form a cluster $(Fe_4P^I{}_4O_{16})$. The clusters are connected with $P^{II}O_4$ tetrahedra to form chains running along the *c* axis. Furthermore, the chains are linked to each other through corner-shared FeO_5−P^IO_4 to form elliptical eight-ring channels, in which potassium ions are located. We note that the elliptical eight-ring channels in the titled material are quite similar to those of natrolite $Na_2Al_2Si_3O_{10}\cdot 2H_2O$ (Figure 1a). However, the elliptical eight-ring channels in natrolite are not a closed but exist in a helical arrangement, corresponding to the space group *Fdd*2. One of the most remarkable differences is seen in the chains running along the *c* axis, showing that the building $Fe_4P_5O_{20}$ units of $K_4Fe_4P_5O_{20}$ follow the 4 = 4 = 1 type of $\{-(P^{II}O_4){=}(2FeO_5{-}2P^IO_4){=}(2FeO_5{-}2P^IO_4){=}(P^{II}O_4)-\}_\infty$, while the $Al_2Si_3O_{10}$ units of $Na_2Al_2Si_3O_{10}\cdot 2H_2O$ are the 4 = 1 type of $\{-(Si^{II}O_4){=}(2AlO_4{-}2Si^IO_4){=}(Si^{II}O_4)-\}_\infty$. Although the polyhedra in their frameworks connect to each other by corner-sharing, a difference in the linkage of polyhedra is clearly seen, where all of the PO_4 in $K_4Fe_4P_5O_{20}$ connect to FeO_5 (PO_4−FeO_5−PO_4) via a corner-sharing oxygen atom, whereas the connection of SiO_4 and SiO_4 (Si^IO_4−$Si^{II}O_4$) exists in $Na_2Al_2Si_3O_{10}\cdot 2H_2O$. Such a difference may be due to the ratio of Si/Al = 1.5 in $Na_2Al_2Si_3O_{10}\cdot 2H_2O$ and P/Fe = 1.25 in $K_4Fe_4P_5O_{20}$, according to Loewenstein's rule.[24]

To check the zeolitic behaviors of $K_4Fe_4P_5O_{20}$, the experiments of gas sorption using N_2 (the dynamic diameter Φ3.64 Å) and H_2 (Φ2.89 Å) were carried out at 77 K. Except for a little surface absorption, almost no N_2 gas sorption is seen in the N_2 sorption isotherms (Figure 2a). Considering that N_2 belongs to one of the larger gas molecules, this is thus in good agreement with the sorption properties of microporous compounds such as natrolite analogues with a small pore size that is also crowded with the cations such as K^+ or Na^+.[25] For one of the smallest gases, H_2, a linear increase in the uptake with increasing pressure is however seen in the H_2 sorption isotherms (Figure 2b), confirming the reversible sorption behavior of $K_4Fe_4P_5O_{20}$. Since the channels (∼10.01 × 3.76 Å^2) in $K_4Fe_4P_5O_{20}$ are smaller than that (∼10.01 × 4.89 Å^2) in $Na_2Al_2Si_3O_{10}\cdot 2H_2O$, whereas the radius of K^+ located inside the channels is larger than that of Na^+, it is reasonable that $K_4Fe_4P_5O_{20}$ exhibits less pronounced sorption behaviors compared to $Na_2Al_2Si_3O_{10}\cdot 2H_2O$.

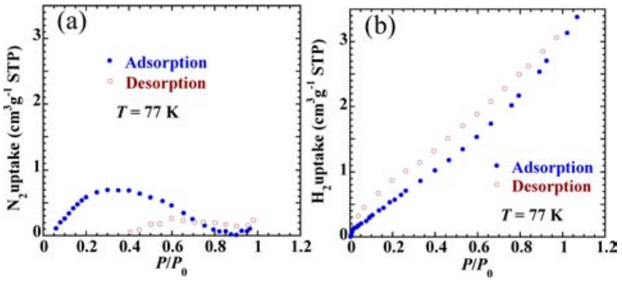

Figure 2. The gas sorption isotherms of $K_4Fe_4P_5O_{20}$ at 77 K. (a) N_2 and (b) H_2. P/P_0 is the ratio of gas pressure (P) to saturated pressure (P_0) with P_0 = 760 mmHg.

To confirm mixed valence Fe ions in $K_4Fe_4P_5O_{20}$, magnetic and ^{57}Fe Mössbauer measurements were performed. Figure 3a shows the temperature dependence of the magnetic susceptibilities measured in an applied field of 0.1 T. The susceptibilities increase with decreasing temperature, and typical Curie−Weiss behavior is observed above 30 K, giving the Curie constant C = 16.538 emu K/mol and Weiss constant θ = −107.02 K. The effective magnetic moment (μ_{eff}) is calculated to be 5.751 μ_B, which is larger than the value of 4.899 μ_B for S = 2 (high spin state of Fe^{2+} ions) and smaller than that of 5.916 μ_B for S = 5/2 (high spin state of Fe^{3+} ions) with a g factor of 2, showing a mixed valence of Fe^{2+}/Fe^{3+} in the system. Figure 3b shows the ^{57}Fe Mössbauer spectrum measured at room temperature. The spectrum consists of paramagnetic doublets which are assigned to high-spin Fe^{3+} (isomer shift of ∼0.5 mm/s) and Fe^{2+} ions (that of ∼1.3 mm/s).[26] The area ratio of the two doublets (Fe^{3+}/Fe^{2+}) is about 76:24 (as seen in Table S6, Supporting Information), agreeing with the occupation of 3/4 Fe^{3+} and 1/4 Fe^{2+} ions in $Fe_4P_5O_{20}$ units

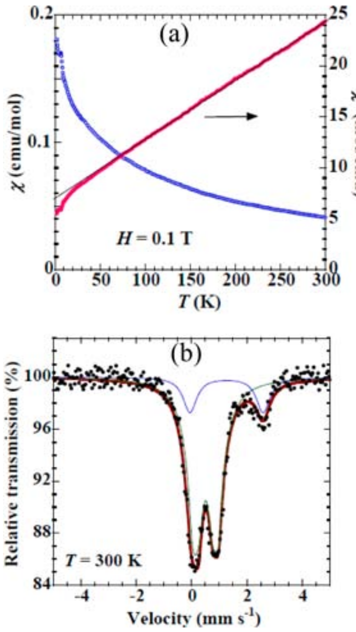

Figure 3. (a) The temperature dependence of the magnetic susceptibilities and the reciprocal one measured in an applied field of 0.1 T. (b) The Mössbauer spectrum measured at room temperatures, where the circles are experimental data and the lines are the fits using a Lorentzian function.

suggested by structural analysis. The results give concrete evidence for mixed valence iron ions in the titled material.

In summary, a new microporous compound $K_4Fe_4P_5O_{20}$ with a natrolite-like framework was obtained by conventional high-temperature solid-state reaction in a closed alumina crucible. Unlike the natrolite family, Fe ions in a framework have trigonal-bipyramid instead of tetrahedral oxygen-coordination. The reversible H_2 gas sorption behaviors were confirmed, showing less pronounced sorption abilities owing to small channels that are also crowded with the large K^+ ions. Furthermore, our experimental results combined from magnetic susceptibility and ^{57}Fe Mössbauer spectrum measurements confirmed mixed valence Fe^{3+}/Fe^{2+} ions in $K_4Fe_4P_5O_{20}$. The present results would open a new route to search for transition-metal-containing microporous materials with a high-temperature solid-state reaction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The detailed experiments and structural and Mössbauer spectral parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hezz@fjirsm.ac.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Professor Jian Zhang in FJIRSM for his help with gas sorption experiments. This work was financially supported by the NSFC (Grant No. 11074250), the National Basic Research Program of China (No. 2012CB921701), the NSF of Fujian Province (2010J01019), and Program for Excellent Talents in Fujian Province.

■ REFERENCES

(1) Klaproth, M. H. *Ges. Naturforsch. Freunde Berlin, Neue Schrifl.* **1803**, *4*, 243.

(2) Pauling, L. *Proc. Natl. Acad. Sci. U. S. A.* **1930**, *16*, 453.

(3) Taylor, W. M.; Meek, C. A.; Jackson, W. W. *Z. Kristallogr.* **1933**, *84*, 373.

(4) Meir, W. M. *Z. Kristallogr.* **1960**, *113*, 430.

(5) Stuckenschmidt, E.; Joswig, W.; Baur, W. H. *Phys. Chem. Miner.* **1994**, *21*, 309.

(6) Ghermani, N. E.; Lecomte, C.; Dusausoy, Y. *Phys. Rev. B* **1996**, *53*, 5231.

(7) Lee, Y.; Hriljac, J. A.; Kim, S. J.; Hanson, J. C.; Vogt, T. *J. Am. Chem. Soc.* **2003**, *125*, 6036.

(8) Lee, Y.; Kim, S. J.; Kao, C.-C.; Vogt, T. *J. Am. Chem. Soc.* **2009**, *131*, 7554.

(9) Lee, Y.; Vogt, T.; Hriljac, J. A.; Parise, J. B.; Artioli, G. *J. Am. Chem. Soc.* **2002**, *124*, 5466.

(10) Lee, Y.; Vogt, T.; Hriljac, J. A.; Parise, J. B.; Hanson, J. C.; Kim, S. J. *Nature* **2002**, *420*, 485.

(11) Lee, Y.; Lee, Y.; Seoung, D. *Am. Mineral.* **2010**, *95*, 1636.

(12) Shin, J.; Bhange, D. S.; Camblor, M. A.; Lee, Y.; Kim, W. J.; Nam, I.-S.; Hong, S. B. *J. Am. Chem. Soc.* **2011**, *133*, 10587.

(13) Hill, G. L.; Bailey, E.; Stennett, M. C.; Hyatt, N. C.; Maddrell, E. M.; McMillan, P. F.; Hriljac, J. A. *J. Am. Chem. Soc.* **2011**, *133*, 13883.

(14) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 1146.

(15) Bu, X.; Feng, P.; Gier, T. E.; Zhao, D.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 13389.

(16) Feng, P.; Bu, X.; Stucky, G. D. *Angew. Chem., Int. Ed.* **2009**, *48*, 6647.

(17) Vaughan, D. E. W.; Yennawar, H. P.; Perrotta, A. J. *Chem. Mater.* **2006**, *18*, 3611.

(18) Baerlocher, C.; McCusker, L. B.; Olson, D. H. *Atlas of Zeolite Framework Types*, 6th ed.; Elsevier: Amsterdam, 2007.

(19) Bellussi, G.; Rigutto, M. S. *Innovation in Zelolite Materials Science*; Elsevier: Amsterdam, 1994; pp 177−213.

(20) Feng, P.; Bu, X.; Stucky, G. D. *Nature* **1997**, *388*, 735.

(21) Pauling, L. *J. Am. Chem. Soc.* **1929**, *51*, 1010−1026.

(22) Dyer, A.; Faghihian, H. *Microporous Mesoporous Mater.* **1998**, *21*, 27.

(23) Crystal data of $K_4Fe_4P_5O_{20}$: Mr = 854.65, tetragonal, $P\bar{4}2c$ with $a = 9.7450(7)$ Å, $c = 9.3800(9)$ Å, $V = 890.77(12)$ Å^3, $Z = 2$, $\rho = 3.186$ g cm^{-3}, F(000) = 830, $\mu = 4.521$ mm^{-1}, $T = 293(2)$ K. A total of 6606 reflections were collected in the range $2.96° < 2\theta < 27.47°$. The final least-squares refinements converged at R1 (wR2) = 0.0466 (0.1272) and $F^2 = 1.096$ for 1015 reflections and 75 parameters with $I > 2\sigma(I)$.

(24) Loewenstein, W. *Am. Mineral.* **1954**, *39*, 92.

(25) Breck, D. W. *Zeolite Molecular Sieves*; Wiley: New York, 1974; p 636.

(26) Hermann, R. P.; Hatert, F.; Fransolet, A.-M.; Long, G. L.; Grandjean, F. *Solid State Sci.* **2002**, *4*, 507.