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LETTER

Synthesis and Characterization of a New Aluminophosphate with $Al_3P_6O_{24}^{9-}$ Three-dimensional Framework†

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Ying Wang,[a,b] Shilie Pan,*[a] Shujuan Han,[a] Lingyun Dong,[a,b] Min Zhang[a] and Kui Wu[a]

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A novel mixed-alkali metal aluminophosphate, $K_6Na_3Al_3P_6O_{24}$ has been successfully synthesized and structurally characterized. The compound contains a unique $Al_3P_6O_{24}^{9-}$ three-dimensional framework composed of AlO_4 and PO_4 tetrahedra with an Al/P ratio of 1/2. This compound melts congruently and is optically transparent from 352 to 2600 nm.

Aluminophosphates (AlPOs) have long been an active area of research, for their widespread applications in catalysis, separation, and ion-exchange reactions.[1] AlPOs that built up of alternation of AlO_n (n= 4, 5, 6) polyhedra and $P(O_b)_n(O_t)_{4-n}$ (b, bridging; t, terminal; n=1, 2, 3, 4) tetrahedra not only show rich compositional and structural varieties with clusters, chains, layers, and open frameworks, but also exhibit unique chemicophysical properties. In the past few years, leading by the discovery of zeolite-like microporous $AlPO_4$-n (n denotes a specific structure type),[2] there is extensive current interest in developing new AlPOs compounds. In this family, it is noticed that the Al/P ratios play an important role on both crystal dimensionalities and structural types, and various stoichiometries of AlPOs with different Al/P ratios and architectures have been systematically reviewed.[3]

Among the AlPOs with three-dimensional (3D) frameworks, many distinct stoichiometries have been found, *i.e.*, $Al_2P_3O_{12}^{3-}$,[4] $Al_4P_5O_{20}^{3-}$,[5] $Al_5P_6O_{24}^{3-}$,[6] $Al_{11}P_{12}O_{48}^{3-}$,[7] and $Al_{12}P_{13}O_{52}^{3-}$,[8] etc. However, in the case of AlPOs with an Al/P ratio of 1/2, few compounds were reported containing 3D frameworks.[9] For example, $AlP_2O_8^{3-}$ generally forms low-dimensional (chains or layers) anionic structures,[10] although recent researches show that $AlP_2O_8^{3-}$ chains may assemble to 3D open frameworks through the connection of transition metal cations.[11] In addition, most of AlPOs are prepared typically by hydrothermal treatment containing templating amine or quaternary ammonium species,[12] nevertheless, 3D framework AlPOs may also be facilitated by inorganic cations in some case.[1d, 3d]

In this work, by using a simple solid state reaction, we have successfully obtained a new compound, $K_6Na_3Al_3P_6O_{24}$ with an Al/P ratio of 1/2, without any separate organic templates. The structure of this compound contains a unique $Al_3P_6O_{24}^{9-}$ 3D framework.

Colorless block crystals of $K_6Na_3Al_3P_6O_{24}$ were synthesized by spontaneous crystallization from stoichiometric composition melt. The single-crystal X-ray diffraction (XRD) analysis reveals that $K_6Na_3Al_3P_6O_{24}$ crystallizes in the monoclinic system with the space group of $P2_1/c$. The structure of $K_6Na_3Al_3P_6O_{24}$ features a unique 3D framework composed of $Al_3P_6O_{24}^{9-}$ anionic structure (Figure 1). In connectivity terms, the structure of $K_6Na_3Al_3P_6O_{24}$ may also be written as $[3(AlO_{4/2})^-6(PO_{2/2}O_{2/1})^-]^{9-}$ with the charge balanced by the Na^+ and K^+ cations. The complicate $Al_3P_6O_{24}^{9-}$ anionic structure consists of three crystallographically distinct Al sites and six crystallographically distinct P sites. In order to simplify the discussion, the disordered O(5A) and O(5B), O(6A) and O(6B) atoms are simplified into two "pseudo-atoms": O(5) and O(6), respectively (Figure S1 in the ESI.†). In this case, all Al and P atoms are tetrahedrally coordinated with Al−O distances varying in the range of 1.665(2) − 1.749(4) Å and P−O distances ranging from 1.490(5) to 1.605(2) Å, respectively. Each AlO_4 tetrahedron is linked to four different PO_4 tetrahedra through its terminal O atoms, while each PO_4 tetrahedron only shares its two vertices with two neighboring AlO_4 tetrahedra, and the other two corners are free. The Al-O-Al or P-O-P connections are not observed in this structure, which obeys the Lowenstein's rule.[13] In addition, based on bond valence calculations,[14] the bond valence sums (BVS) for Al and P atoms are in the range of 3.1-3.2 and 4.8-4.9, in accordance with their normal valences +3 and +5, respectively.

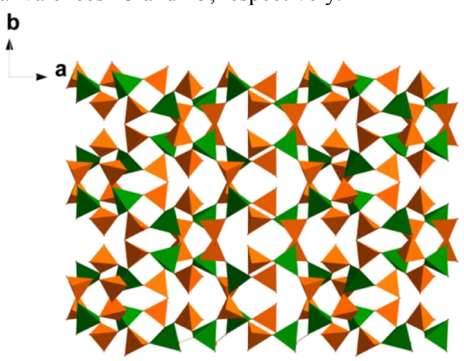

Figure 1. View of $Al_3P_6O_{24}^{9-}$ 3D framework (AlO_4, green; PO_4, orange)

Traditionally, if all Al and P atoms in AlPOs are four coordinated with oxygen and linked with each other alternately forming 3D frameworks, this type of AlPOs show many structural and compositional similarities compared to aluminosilicate zeolites.[2, 3b] Some interrupted 3D AlPOs have been previously reported with zeolite-like structures; however, to the best of our knowledge, this type of $Al_3P_6O_{24}^{9-}$ anionic framework with an Al/P ratio of 1/2 has never been reported, and we could not find any similar prototype in zeolites.[15] To simplify such a 3D architecture, a topological approach is applied. By considering the Al(1), Al(2) and Al(3) atoms as 4-connected nodes (Figure 2), the anionic partial structure can be rationalized as a 3-nodal topological net with the Schläfli symbol of $(6.8^5)(6^2.8)(8^3)$. This framework reported herein defines a new topology according to TOPOS database,[16] which further confirms that it is a new structural type in AlPOs.

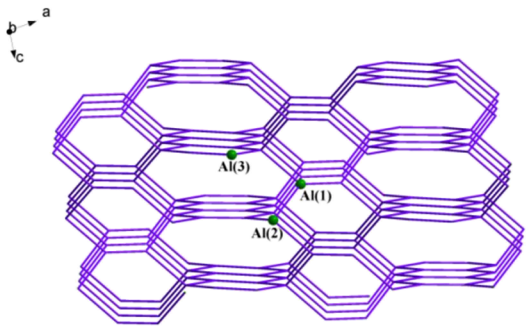

Figure 2. View of the 3-nodal topological network with the Schläfli symbol of $(6.8^5)(6^2.8)(8^3)$

There are three crystallographically unique Na atoms, which are located in the $Al_3P_6O_{24}^{9-}$ framework and the Na-O bonds distances range from 2.211(3) to 2.648(3) Å. Six crystallographically unique K atoms are found in the channels of $Al_3P_6O_{24}^{9-}$ anionic framework along the [1 0 $\bar{1}$] direction, with the K-O bonds distances range from 2.508(3) to 3.422(4) Å (Figure 3a). The channel could be recognized as infinite loop–branched helices built of alternatively distorted AlO_4 and PO_4 tetrahedra (Figure 3b). It is interesting that only K atoms are located in this channel, while all Na atoms fill in the other void of the anionic framework. The reason may be simply explained by the

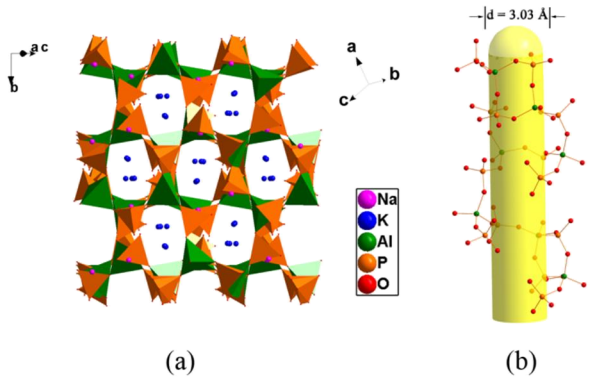

Figure 3. (a) View of the channel of $Al_3P_6O_{24}^{9-}$ framework along the [1 0 $\bar{1}$] direction; (b) Structure details of the infinite loop–branched helices. The channel diameter (expressed as the shortest O-O distance) is 3.03 Å.

different ionic radius and coordinate numbers between Na^+ and K^+. It also indicates that cations may have the structure-directing role in the crystallization process of $K_6Na_3Al_3P_6O_{24}$. Besides, in order to quantify the "openness" of $Al_3P_6O_{24}^{9-}$ framework, the amount of void space is quantitatively calculated by removing all of the non-framework atoms, Na^+ and K^+, using the *CALC SOLV* command in PLATON.[17] For $K_6Na_3Al_3P_6O_{24}$, the amount of void space is 6.4% (5.2% for removing K^+ cations only). The void space becomes zero when all cations are included in this calculation. The result suggests that although $K_6Na_3Al_3P_6O_{24}$ has a 3D framework, the amount of void space is comparably small, that is to say, its 3D framework has a low degree of openness. BVS for Na and K atoms are in the range of 1.0-1.2 and 0.9-1.1, respectively, indicating that the coordinate environments of cations are all reasonable.

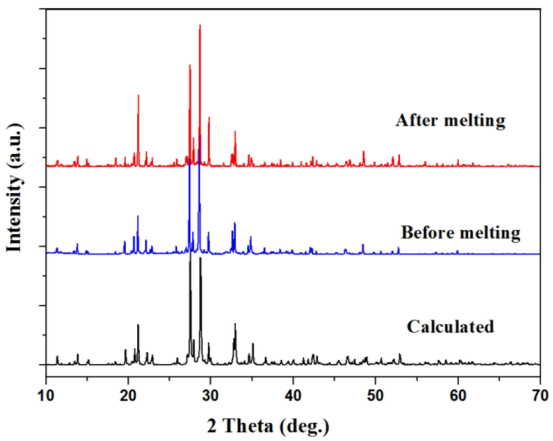

Figure 4. Powder XRD patterns of calculated, before melting and after melting.

Polycrystalline samples of $K_6Na_3Al_3P_6O_{24}$ were synthesized via standard solid-state reactions, and the powder XRD patterns of the as-synthesized samples show good agreement with the calculated one derived from the single-crystal data (Figure 4). Thermal gravimetric analysis (TGA) performed on polycrystalline samples of $K_6Na_3Al_3P_6O_{24}$ exhibits no weight loss up to 1000 °C (Figure S2 in the ESI.†). Meanwhile, only one endothermic peak (at 884 °C) is observed in the heating curves of the differential scanning calorimetry (DSC) results, which was later confirmed to be the melting point. In addition, to verify the crystallization process, polycrystalline samples of $K_6Na_3Al_3P_6O_{24}$ were melted at a temperature above 900 °C and then cooled down to 800 °C at a rate of 5 °C/h, followed by a rapid cooling to room temperature. Analysis of the powder XRD pattern of the solidified melt reveals that the solid product is identical to that of the initial powder (Figure 4). These results demonstrate that $K_6Na_3Al_3P_6O_{24}$ is a congruently melting compound.

The IR spectrum for $K_6Na_3Al_3P_6O_{24}$ displays absorption peaks around 555, 714, 941, 1076 and 1172 cm^{-1}, which are attributed to the characteristic absorptions of AlPOs (Figure S3 in the ESI.†).[18] The UV-Vis-NIR diffuse reflectance spectrum measurements on powder samples exhibit no absorption in the range from 352 to 2600 nm (Figure S4 in the ESI.†).

Many AlPOs are reported to be useful as molecular sieves or ion-exchange hosts.[19] $K_6Na_3Al_3P_6O_{24}$ has a 3D framework structure and channels along the [1 0 $\bar{1}$] direction; therefore, it may be able to

undergo ion-exchange reactions. The polycrystalline samples of $K_6Na_3Al_3P_6O_{24}$ (ca. 1g) were stirred in 30 mL of $LiNO_3$ (~1 M) aqueous solution for 1 day at 50 °C and then an additional 10 days at room temperature. The exchanged samples were washed repeatedly with deionized water and ethanol and then air-dried. The exchanged samples were further investigated by ICP analysis, and the results show that the replacement of K^+ ions by Li^+ ion was not successful. Meanwhile, the powder XRD results reveal that the material transforms from highly crystalline phase to amorphous phase after treatment (Figure S5 in the ESI.†). It indicates that the 3D framework of $K_6Na_3Al_3P_6O_{24}$ may collapse during solution reactions, which make ion-exchange experiments unsuccessful.

In summary, a new mixed-alkali metal AlPO $K_6Na_3Al_3P_6O_{24}$, has been prepared by solid state reaction. The compound enriches the family of AlPOs: it contains the novel $Al_3P_6O_{24}^{9-}$ 3D framework with an Al/P ratio of 1/2. This compound melts congruently at 884 °C and has a wide optically transparent range from 352 to 2600 nm. We are expecting to prepare more AlPOs with similar structural features in due time.

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Experimental

Polycrystalline samples of $K_6Na_3Al_3P_6O_{24}$ were synthesized via solid-state reactions of the stoichiometric starting components (0.02mol) of $NaNO_3$ (99.0%), KNO_3 (99.0%), $Al(NO_3)_3{\cdot}9H_2O$ (99.0%) and $NH_4H_2PO_4$ (99.5%). The single crystals were grown by spontaneous crystallization from the melt of polycrystalline samples (5g). The experimental details are to be found in the ESI.†

Notes and references

[a] Key Laboratory of Functional Materials and Devices for Special Environments of CAS, Xinjiang Technical Institute of physics & Chemistry of CAS, Xinjiang Key Laboratory of Electronic Information Materials and Devices, 40–1 South Beijing Road, Urumqi 830011, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
* To whom correspondence should be addressed
E-mail: slpan@ms.xjb.ac.cn (Shilie Pan) Tel: (86)-991-3674558 Fax: (86)-991-3838957

† Crystal data (CCDC: 969011): Monoclinic, space group $P2_1/c$, a = 19.9204(16) Å, b = 9.6139(8) Å, c = 13.2845(11) Å, β = 98.934(4)°, V = 2513.3(4) Å^3, Z = 4, D_c = 2.522 g/cm^3, μ = 1.683 mm^{-1}, F (000) = 1872, GOF = 1.047, R_1 = 0.0370 and wR_2 = 0.1033 ($F_o^2 \geq 2\sigma(F_o^2)$). Electronic Supplementary Information (ESI) available: [The experimental details, crystallographic data, atomic coordinates and isotropic displacement coefficients, important bond distances, IR spectrum, UV-Vis-NIR optical diffuse reflectance spectrum, thermal analysis and XRD result of ion-exchange experiment are presented]. See DOI: 10.1039/c000000x/

1 (a) A. K. Cheetham, G. Férey, T. Loiseau, *Angew. Chem. Int. Ed.* 1999, **38**, 3268-3292; (b) J. M. Thomas, R. Raja, G. Sankar, R. G. Bell, D. W. Lewis, *Pure Appl. Chem.* 2001, **73**, 1087 -1101; (c) C. Baerlocher, L. B. McCusker, D. H. Olson, *Atlas of Zeolite Framework Types*, 6 ed., Elsevier, 2007; d) M. Hartmann, L. Kevan, *Chem. Rev.* 1999, **99**, 635-664.
2 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan, E. M. Flanigen, *J. Am. Chem. Soc.* 1982, **104**, 1146-1147.
3 (a) N. Rajić, *J. Serb. Chem. Soc.* 2005, **70**, 371-391; (b) E. M. Flanigen, B. M. Lok, R. L. Patton, S. T. Wilson, *Pure Appl. Chem.* 1986, **58**, 1351-1358; (c) S. Oliver, A. Kuperman, G. A. Ozin, *Angew. Chem. Int. Ed.* 1998, **37**, 46-62; (d) J. H. Yu, R. R. Xu, *Acc. Chem. Res.* 2003, **36**, 481-490.
4 B. Wei, G. S. Zhu, J. H. Yu, S. L. Qiu, F. S. Xiao, O. Terasaki, *Chem. Mater.* 1999, **11**, 3417-3419.
5 J. Yu, K. Sugiyama, S. Zheng, S. Qiu, J. Chen, R. Xu, Y. Sakamoto, O. Terasaki, K. Hiraga, M. Light, M. B. Hursthouse, J. M. Thomas, *Chem. Mater.* 1998, **10**, 1208-1211.
6 Q. S. Huo, R. R. Xu, S. G. Li, Z. G. Ma, J. M. Thomas, R. H. Jones, A. M. Chippindale, *J. Chem. Soc., Chem. Commun.* 1992, 875-876.
7 W. F. Yan, J. H. Yu, Z. Shi, P. Miao, K. X. Wang, Y. Wang, R. R. Xu, *Micropor. Mesopor. Mat.* 2001, **50**, 151-158.
8 W. Yan, J. H. Yu, R. R. Xu, G. S. Zhu, F. S. Xiao, Y. Han, K. Sugiyama, O. Terasaki, *Chem. Mater.* 2000, **12**, 2517-2519.
9 W. F. Yan, J. H. Yu, Z. Shi, R. R. Xu, *Chem. Commun.* 2000, 1431-1432.
10 (a) I. D. Williams, J. H. Yu, Q. M. Gao, J. S. Chen, and R. R. Xu, *Chem. Commun.*, 1997, 1273–1274; (b) R. H. Jones, J. M. Thomas, R. R. Xu, Q. S. Huo, Y. Xu, A. K. Cheetham, and D. Bieber, *J. Chem. Soc. Chem. Commun.*, 1990, 1170-1172.
11 (a) K. X. Wang, J. H. Yu, C. J. Li, R. R. Xu, *Inorg. Chem.* 2003, **42**, 4597-4602; (b) K. X. Wang, J. H. Yu, Y. Song, R. R. Xu, *Dalton Trans.* 2003, 99-103.
12 (a) L. Wang, Y. P. Xu, Y. Wei, J. C. Duan, A. B. Chen, B. C. Wang, H. J. Ma, Z. J. Tian, L. W. Lin, *J. Am. Chem. Soc.* 2006, **128**, 7432-7433; (b) A. K. Paul, S. Natarajan, *Cryst. Growth Des.* 2010, **10**, 765-774.
13 W. Lowenstein, *Am. Mineral.* 1954, **39**, 92.
14 (a) I. D. Brown, D. Altermatt, *Acta Crystallogr., Sect. B: Struct. Sci.* 1985, **41**, 244-247; (b) N. E. Brese, M. O'Keeffe, *Acta Crystallogr., Sect. B: Struct. Sci.* 1991, **47**, 192-197.
15 (a) M. Estermann, L. B. McCusker, C. Baerlocher, A. Merrouche, and H. Kessler, *Nature*, 1991, **352**, 320–323; (b) R. C. Rouse and D. R. Peacor, *Am. Mineral.*, 1994, **79**, 175–184; (c) J. H. Yu and R. R. Xu, *Chem. Soc. Rev.*, 2006, **35**, 593–604.
16 V. A. Blatov, *Struct. Chem.* 2012, **23**, 955-963.
17 A. L. Spek, *J. Appl. Crystallogr.* 2003, **36**, 7-13.
18 U. Shayachmetov, R. Shayachmetov, I. Dranca, *Int. J. Thermophys.* 2001, **22**, 979-993.
19 (a) X. W. Song, Y. Li, L. Gan, Z. P. Wang, J. H. Yu, and R. R. Xu, *Angew. Chem. Int. Ed.*, 2009, **48**, 314–7; (b) K. G. Varshney, A. H. Pandith, and U. Gupta, *Langmuir*, 1998, **14**, 7353–7358; (c) B. T. Holland, P. K. Isbester, C. F. Blanford, E. J. Munson, and A. Stein, *J. Am. Chem. Soc.*, 1997, **119**, 6796–6803.

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