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LETTERS TO THE EDITOR

Synthesis and Structure of a Novel Microporous Crystal $AlPO_4$–CJ_2

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A novel microporous crystal, $AlPO_4$–CJ_2, is hydrothermally synthesized. Single crystal X-ray diffraction shows that it is a novel aluminophosphate crystal with an open framework. It crystallizes in space group $P_{2_12_12_1}$ with a = 9.456(3), b = 9.621(5), and c = 9.965(5) Å and V = 906.6(7) Å^3. The crystal structure has been refined to R_w = 0.045. The framework structure consists of AlO_5, AlO_5F, and PO_4 units. The three-dimensional framework constructed by Al, P, O, and F atoms has two kinds of open channels. One is formed by 8-T rings packing along [100], the other is formed by zigzag packing of 8-T rings along [001].

Introduction

Microporous crystalline inorganic solids are known to be very useful materials for catalysis, adsorption, and ion exchange. The aluminophosphate crystals as molecular sieves synthesized by a novel method from gels in the presence of organic amines and quaternary ammonium species (*1*). The new family of aluminophosphates contains about two dozen three-dimensional framework structures, most of which are microporous, and some two-dimensional layer-type materials. To date, the structures of several "as-synthesized" materials have been published (*2–8*). Recently many new aluminophosphates with novel structures have been synthesized (*9*). We report here the synthesis and structure of a novel aluminophosphate with an open framework, known as $AlPO_4$–CJ_2.

Synthesis

Hydrothermal crystallization of a reaction mixture with molar composition 1.0 Al_2O_3 : 1.0 P_2O_5 : 2.0 NH_4F : 1.0 hexamethylenetetramine: 40 H_2O was carried out in a stainless steel autoclave lined with polytetrafluoroethylene under autogenous pressure at 150°C for 23 hr. The crystalline product was filtered, washed with distilled water, and dried at ambient temperature. Excellent single crystals suitable for structural analysis by X-ray diffraction could be selected readily.

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TABLE I

ATOM COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS (Å$^2 \times 10^3$)

Atom	X	Y	Z	U
P(1)	4,237(2)	2086(1)	3574(1)	8(1)[a]
P(2)	9,200(2)	−149(1)	3611(1)	9(1)[a]
Al(1)	6,031(2)	2367(2)	6396(2)	8(1)[a]
Al(2)	6,529(2)	246(2)	1767(2)	8(1)[a]
O(1)	4,316(5)	3488(4)	2834(4)	11(1)[a]
O(2)	7,649(4)	234(4)	3361(3)	13(1)[a]
O(3)	5,502(5)	315(4)	124(3)	12(1)[a]
O(4)	4,896(5)	2193(4)	4981(4)	16(1)[a]
O(5)	10,196(5)	952(4)	3013(4)	13(1)[a]
O(6)	5,440(5)	1556(4)	7923(3)	11(1)[a]
O(7)	4,951(5)	973(4)	2747(3)	11(1)[a]
O(8)	2,677(5)	1646(4)	3773(4)	13(1)[a]
O(9)	6,936(4)	689(4)	5925(3)	9(1)[a]
O(10)	2,437(6)	856(5)	6852(5)	39(2)[a]
O(11)	4,775(7)	3381(6)	54(5)	51(2)[a]
F(1)	7,210(4)	1978(3)	1370(4)	17(1)[a]

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U tensor.

Determination of the Structure

A colorless crystal was mounted in an R3 computer automatized four-circle diffractometer. The lattice constants at 296 K were measured with Mo $K\alpha$ (λ = 0.71069 Å, graphite monochromator) on the basis of α_1 automatically centered reflections: orthorhombic system, a = 9.456(3), b = 9.621(5), c = 9.965(5) Å, V = 906.6(7) Å^3. Intensities were collected by means of the ω-scan technique with variable scan rate from 5.0 to 29.3° min^{-1} in the range of $3° < 2\theta < 70°$. A total of 2870 reflections was measured, of which 1316 with $|F| > 4.0\sigma(|F|)$ were considered unique and used for structure refinements. The data were reduced by applying $L\,P$, K(overall scale), and B(overall isotropic temperature) factors. We calculate to obtain absolute intensities and determine the space group is $P_{2_12_12_1}$ uniquely.

The positions of the P and Al atoms in an asymmetric unit were determined from direct method calculation, and several cycles of subsequent electron density syntheses yielded the location of all remaining nonhydrogen atoms. Cascade matrix block-diagonal least-squares refinements of position coordinates and anisotropic thermal parameters of all nonhydrogen atoms gave the final R = 0.059 and R_w = 0.045, respectively. All calculations were made with the SHELXTL program system and an Eclipse S/250 computer.

Description of the Structure and Discussion

The nonhydrogen atomic coordinates and equivalent thermal parameters (U_{eq}), interatomic distances, and angles are listed in Tables I, II, and III, respectively.

In the asymmetric unit of the $AlPO_4$–CJ_2 structure (Fig. 1), each P atom is strictly tetrahedrally coordinated by the four closest oxygen atoms. The P–O distances are in the range of 1.511–1.556 Å, and O–P–O angles, from 106.7 to 111.3°. In the asymmetric unit one Al is five-coordinated and the other is six-coordinated. The former is located in a distorted trigonal bipyramid and the latter lies in a distorted octahedron. It is of considerable interest that the Al (2) atom not only is coordinated by five framework oxygen

TABLE II

BOND LENGTHS (Å)

P(1)–O(1)	1.539(4)	P(1)–O(4)	1.538(4)
P(1)–O(7)	1.511(4)	P(1)–O(8)	1.547(5)
P(2)–O(2)	1.532(5)	P(2)–O(5)	1.537(4)
P(2)–O(3a)	1.542(4)	P(2)–O(6a)	1.556(4)
Al(1)–O(4)	1.780(5)	Al(1)–O(6)	1.798(4)
Al(1)–O(9)	1.886(4)	Al(1)–O(5a)	1.893(4)
Al(1)–O(8a)	1.831(5)	Al(2)–O(2)	1.910(4)
Al(2)–O(3)	1.905(4)	Al(2)–O(7)	1.915(5)
Al(2)–F(1)	1.829(4)	Al(2)–O(1a)	1.913(4)
Al(2)–O(9a)	1.903(4)	O(1)–Al(2a)	1.913(4)
O(3)–P(2a)	1.543(4)	O(5)–Al(1a)	1.893(4)
O(6)–P(2b)	1.555(4)	O(8)–A1(1b)	1.831(5)
O(9)–A1(2b)	1.903(4)		

TABLE III
BOND ANGLES (°)

O(1)–P(1)O(4)	111.0(2)	O(1)–P(1)–O(7)	109.7(2)
O(4)–P(1)–O(7)	111.3(2)	O(1)–P(1)–O(8)	110.3(2)
O(4)–P(1)–O(8)	106.7(2)	O(7)–P(1)–O(8)	107.6(2)
O(2)–P(2)–O(5)	111.0(2)	O(2)–P(2)–O(3a)	111.0(2)
O(5)–P(2)–O(3a)	109.8(2)	O(2)–P(2)–O(6a)	110.3(2)
O(5)–P(2)–O(6a)	107.2(2)	O(3a)–P(2)–O(6a)	107.5(2)
O(4)–Al(1)–O(6)	116.2(2)	O(4)–Al(1)–O(9)	89.8(2)
O(6)–Al(1)–O(9)	88.9(2)	O(4)–Al(1)–O(5a)	94.3(2)
O(6)–Al(1)–O(5a)	88.7(2)	O(9)–Al(1)–O(5a)	175.9(2)
O(4)–Al(1)–O(8a)	119.2(2)	O(6)–Al(1)–O(8a)	124.6(2)
O(9)–Al(1)–O(8a)	92.0(2)	O(5a)–Al(1)–O(8a)	86.6(2)
O(2)–Al(2)–O(3)	176.6(2)	O(2)–Al(2)–O(7)	90.6(2)
O(3)–Al(2)–O(7)	91.6(2)	O(2)–Al(2)–F(1)	89.4(2)
O(3)–Al(2)–F(1)	87.8(2)	O(7)–Al(2)–F(1)	93.0(2)
O(2)–Al(2)–O(1a)	93.0(2)	O(3)–Al(2)–O(1a)	89.8(2)
O(7)–Al(2)–O(1a)	83.8(2)	F(1)–Al(2)–O(1a)	175.9(2)
O(2)–Al(2)–O(9a)	86.6(2)	O(3)–Al(2)–O(9a)	91.5(2)
O(7)–Al(2)–O(9a)	172.6(2)	F(1)–Al(2)–O(9a)	93.9(2)
O(1a)–Al(2)–O(9a)	89.5(2)	P(1)–O(1)–Al(2a)	130.9(2)
P(2)–O(2)–Al(2)	131.9(2)	Al(2)–O(3)–P(2a)	138.0(2)
P(1)–O(4)–Al(1)	166.6(3)	P(2)–O(5)–Al(1a)	136.4(2)
Al(1)–O(6)–P(2b)	133.0(3)	P(1)–O(7)–Al(2)	152.3(3)
P(1)–O(8)–Al(1b)	131.0(2)	Al(1)–O(9)–Al(2b)	129.9(2)

atoms but also is bonded to one F atom, F–Al = 1.829 Å. Eight of the nine framework oxygen atoms are bonded to one P atom and one Al atom, whereas the ninth, representing the position of a water molecule, bridges two Al atoms. There are two sets of Al–O bond lengths in the AlO_5 units. One refers to the distance of Al–O (pyramid apex) having a range of 1.886–1.893 Å and the other refers to the distance of Al–O (nonpyramid apex) having a range of 1.780–1.831 Å.

The three-dimensional network constructed by Al, P, O, and F atoms has two kinds of open channels as shown in Fig. 2 (O and F atoms are omitted for clarity). One is formed by 8-*T* (*T* = Al or P) rings packing along (100), the other is formed by zigzag packing of 8-*T* rings along (001). Topologically, the 3D framework can be viewed as being built of the 2D nets in a certain way. The 2D nets running along (001) are composed of 3 and 8 rings. The sharing-edge of 3 ring and 3 ring is a bridge-oxygen of water molecule. These rings are not coplanar, but rather corrugated. The 2D nets are con-

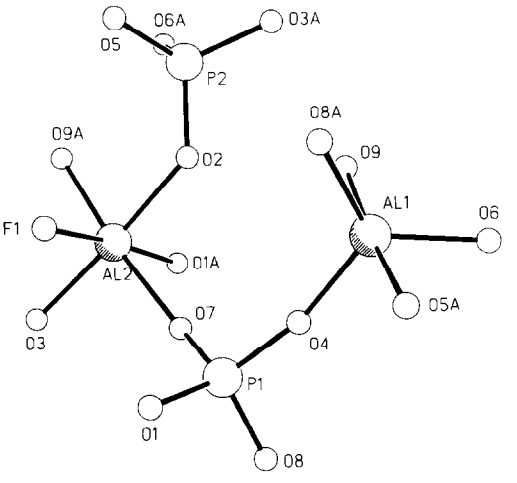

FIG. 1. Connection in an asymmetric unit of $AlPO_4$–CJ_2.

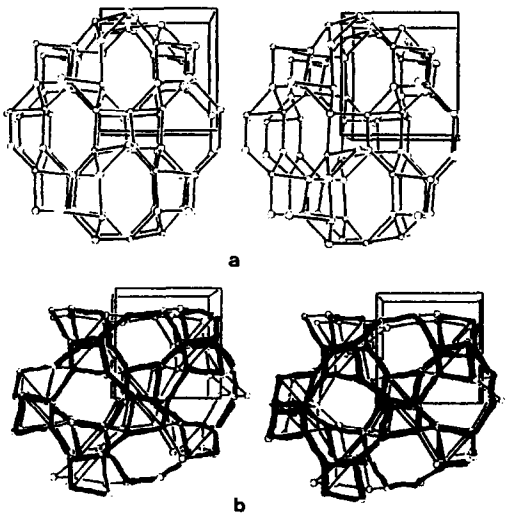

FIG. 2. Stereoview of $AlPO_4$-CJ_2 framework composed of Al and P nodes along (a) (100) and (b) (001). Smaller circle, Al atom; larger circle, P atom.

nected via crankshaft chains to form the 3D framework.

In summary, a novel microporous crystalline aluminophosphate, $AlPO_4$-CJ_2, is hydrothermally synthesized. The framework of a aluminophosphate molecular sieve consists of AlO_5, AlO_5F, and PO_4 units. The three-dimensional framework constructed by Al, P, O, and F atoms has two kinds of open channels.

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