LETTER TO THE EDITOR

The Synthesis and Structure of a Beryllophosphate Crystal with an Open Framework

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A beryllophosphate single crystal with an open framework was hydrothermally synthesized. Structure determination with four-circle X-ray diffraction shows that it crystallizes with the space group $P2_1/a$ (monoclinic), with $a = 9.784(1)$, $b = 7.659(1)$, $c = 4.808(1)$Å, $\beta = 90.05(1)°$, and $V = 360.26$ Å^3. The final discrepancy factor was $R = 0.029$ and $R_w = 0.033$. The crystal consists of PO$_4$ and BeO$_3$OH tetrahedra. There are regular eight-membered rings and four-membered ring channels parallel to the (001) direction in the framework. © 1992 Academic Press, Inc.

Introduction

Since aluminophosphate molecular sieves have been developed by U.C.C. (America) (*1*), the synthesis of binary phosphates with porous structures has been extensively emphasized (*2*). Some novel beryllophosphate crystals with open frameworks have been reported (*3–7*). Here we describe a new beryllophosphate single crystal synthesized by the hydrothermal crystallization method and its structure.

Synthesis

To generate the mole ratio of the reactant mixture, 1.0 BeO : 0.5 P$_2$O$_5$: 1.7 CaCl$_2$: 1.2 TEAOH : 400 H$_2$O (TEAOH, tetraethylene-amine hydroxide), these procedures were followed: First, BeSO$_4$ and H$_3$PO$_4$ were dis-

solved in distilled water. Then CaCl$_2$ and TEAOH were added to the solution, and the reactant mixture was stirred to form a homogeneous gel. The pH value of the reactant mixture was 5.9. The gel was then sealed in a stainless steel autoclave lined with polytetrafluoroethylene and spun under its autogenous pressure at 150°C for 16 days. 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 readily selected.

Determination of the Structure

A colorless and transparent crystal was mounted in an Enraf–Nonius CAD 4 computer-automated four-circle diffractometer. The lattice constants at 296 K were measured with a MoKα ($\lambda = 0.71069$ Å) graphite monochromator on the basis of automati-

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TABLE I

ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC
THERMAL PARAMETERS

Atom	X	Y	Z	B_{eq}
O(1)	0.0396(2)	0.3988(3)	0.2466(5)	0.59(4)
O(2)	0.4585(2)	0.2835(3)	0.6521(5)	0.51(4)
O(3)	0.1935(2)	0.3445(3)	0.6669(5)	0.53(4)
O(4)	0.1428(2)	0.1059(3)	0.3305(5)	0.62(2)
OH	0.3332(2)	0.4123(1)	0.2039(1)	0.61(3)
Ca	0.3309(0)	0.1116(0)	0.9974(1)	0.43(1)
P	0.0815(1)	0.2710(0)	0.4708(1)	0.22(1)
Be	0.3398(3)	0.4140(3)	0.5371(7)	0.42(5)

TABLE II

BOND DISTANCE (Å)

P–O(1)	1.513(3)	Ca–O(1)'	2.375(3)
P–O(2)'	1.543(3)	Ca–O(1)"	2.369(2)
P–O(3)	1.552(3)	Ca–O(2)	2.459(3)
P–O(4)	1.554(3)	Ca–O(3)	2.741(3)
Be–O(2)	1.630(5)	Ca–O(3)'	2.626(3)
Be–O(3)	1.651(4)	Ca–O(4)"	2.439(4)
Be–O(4)'	1.610(4)	Ca–OH'	2.418(3)
Be–OH	1.602(3)	Ca–OH"	2.509(2)

cally centered reflections: indexing was based on the monoclinic system, with $a = 9.784(1)$, $b = 7.659(1)$, $c = 4.808(1)$ Å, $\beta = 90.05(1)°$, and $V = 360.26$ Å^3. Intensities were collected by means of the 2θ-scan technique in the range of $3° \leq 2\theta \leq 65°$. A total of 1023 reflections were measured, of which 927 with $|F| > 4.0 \, \sigma \, |F|$ were considered unique and used for structure refinements. The data were reduced by applying the LP, K(overall scale), and B(overall isotropic temperature) factors. We determined the absolute intensities and found that the space group is $P2_1/a$.

The positions of the atoms in an asymmetric unit were determined by the Patterson and Fourier methods. Cascade matrix block-diagonal least-squares refinements of position coordinates and anisotropic thermal parameters of all the nonhydrogen atoms yielded final values of $R = 0.029$ and $R_w = 0.033$, respectively.

Description of the Structure and Discussion

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

The basic structural building units are the PO_4 and BeO_3OH tetrahedra, and the P and Be atoms present alternatively in the framework.

In the PO_4 tetrahedra, three oxygen atoms O(2), O(3), and O(4) form an oxygen bridge between the P and Be atoms; the fourth oxygen atom O(1) occurs in form of a terminal oxygen. All four oxygen atoms of the PO_4 unit coordinate the cation of the framework structure, i.e., Ca^{2+}. Likewise, in the BeO_3OH tetrahedra, three oxygen atoms O(2), O(3), and O(4) form an oxygen bridge between the P and Be atoms, but the fourth oxygen atom is part of a terminal hydroxyl (OH) (see Tables II and III). The four oxygen atoms of the BeO_3OH unit also coordinate the Ca^{2+} cation of the structure. The

TABLE III

BOND ANGLES (degrees)

O(1)–P–O(2)'	111.4(1)	O(2)–Be–OH	111.2(1)
O(1)–P–O(3)	112.7(1)	O(2)–Be–O(3)	107.1(2)
O(1)–P–O(4)	108.7(0)	O(2)–Be–O(4)'	110.5(3)
O(2)'–P–O(3)	107.9(1)	O(3)–Be–OH	109.7(2)
O(2)'–P–O(4)	109.0(1)	O(4)'–Be–OH	114.0(3)
O(3)–P–O(4)	106.5(1)	O(3)–Be–O(4)'	103.7(2)
P–O(2)'–Be	122.1(1)	P–O(4)–Be	127.7(2)
P–O(3)–Be	120.1(2)	O(1)'–Ca–O(2)	76.3(5)
O(3)–Ca–OH'	81.6(5)	O(1)'–Ca–O(3)	115.0(5)
O(3)–Ca–O(1)"	137.5(9)	O(1)'–Ca–O(4)"	135.6(9)
O(3)–Ca–O(3)'	145.2(6)	O(1)'–Ca–OH'	73.8(5)
O(3)–Ca–OH"	68.6(6)	O(1)'–Ca–O(1)"	76.5(8)
O(4)"–Ca–OH'	75.5(9)	O(1)'–Ca–O(3)'	79.4(9)
O(4)"–Ca–O(1)"	108.6(8)	O(1)'–Ca–OH'	145.2(9)
O(4)"–Ca–O(3)'	60.9(8)	O(2)–Ca–O(3)	60.7(6)
O(4)"–Ca–OH"	76.3(8)	O(2)–Ca–O(4)"	146.7(8)
OH'–Ca–O(1)"	138.9(9)	O(2)–Ca–OH'	113.9(8)
OH'–Ca–O(3)'	72.1(0)	O(2)–Ca–O(1)"	85.5(7)
OH'–Ca–OH'	138.1(1)	O(2)–Ca–O(3)'	151.8(3)
O(1)"–Ca–O(3)'	75.0(1)	O(2)–Ca–OH'	76.7(8)
O(1)"–Ca–OH'	79.8(8)	O(3)–Ca–O(4)"	91.3(1)
O(3)'–Ca–OH'	118.4(2)		

P–O bond changes in the range 1.513–1.554 Å, in which the shortest P–O bond is the distance between the P atom and the terminal oxygen atom. The Be–O bond lengths vary in the range 1.602–1.630 Å, and the shortest Be–O bond is the Be–OH unit (1.602 Å). We can consider the P and Be atoms to be located in distorted tetrahedra, because the $O(1)–P–O(3)$ and $O(1)–P–O(2)'$ angles are larger than the regular tetrahedral angle, and the $O(3)–P–O(4)$ angle is less than the tetrahedral angle; similar results can be found in the BeO_3OH unit (see Table III). For the $CaO_6(OH)_2$ polyhedra, two (OH) are from the terminal oxygen of BeO_3OH, two O atoms are from the terminal oxygen of PO_4, and the others derive from the bridge oxygens of the framework; these are best described as slightly distorted tetragonal antiprisms which share edges to form a sheet of six-membered rings (Fig. 1).

The framework structure consists of sheets of corner-sharing PO_4 and BeO_3OH tetrahedra which form four-membered rings and eight-membered rings. In the eight-membered rings, Ca^{2+} cations are distributed symmetrically and form $CaO_6(OH)_2$ polyhedra, with the adjacent framework oxygen atoms (as discussed above) (see Fig.

FIG. 2. The sheet of the PO_4 and BeO_3OH tetrahedra of the framework in the downward (001) direction.

2). When sheets composed of $CaO_6(OH)_2$ polyhedra are stacked above other sheets composed of PO_4 and BeO_3OH tetrahedra, such that the Ca^{2+} cations are located in a site in the eight-membered rings, the framework structure is generated along the (001) directions. As a result, four-membered rings and eight-membered ring channels parallel to the (001) direction are produced.

References

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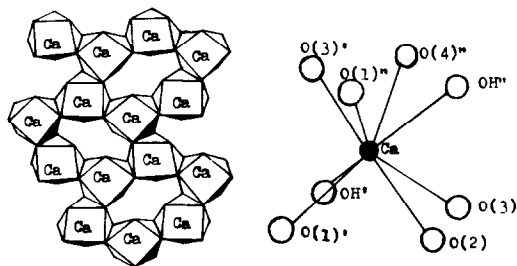7. W. T. A. Harrison et al., J. Mater. Chem. 1, 153 (1991).

FIG. 1. The cation polyhedra sheet of the framework in the downward (001) direction and the coordination diagram of the $Ca^{2+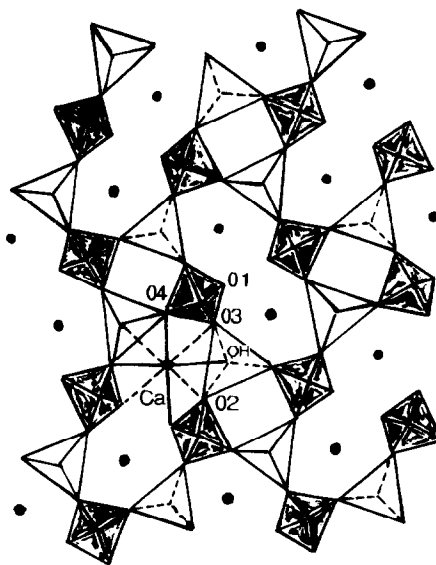}$ cation in the downward (100) direction.