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Crystal structure of paulkellerite

JOEL D. GRICE
Mineral Sciences Division, National Museum of Natural Sciences, Ottawa, Ontario K1P 6P4, Canada
LEE A. GROAT
Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

ABSTRACT

The new mineral species paulkellerite, $Bi_2Fe^{3+}(PO_4)O_2(OH)_2$, is monoclinic, $C2/c$ (No. 15), with Z = 4 and has refined cell parameters $a = 11.380(3)$, $b = 6.660(3)$, $c = 9.653(3)$ Å, and $\beta = 115.34(2)°$. This unique structure was solved by direct methods, then refined by difference-Fourier synthesis, using 858 observed $[>3\sigma(I)]$ reflections, to residuals R = 3.4% and R_w = 3.3%. It has a (100) layered structure with sheets of BiO_7 polyhedra interspersed with layers of P tetrahedra and Fe^{3+} octahedra. The P and Fe^{3+} polyhedra alternate in corner sharing, single chains that parallel the **c** axis.

INTRODUCTION

Paulkellerite, a new mineral species from the Neuhilfe mine, Schneeberg, East Germany, has been described by Dunn et al. (1988). In that description it was noted that the unit-cell parameters and X-ray powder-diffraction data were unique, not resembling those of any other known mineral. The chemical formula of paulkellerite, $Bi_2Fe^{3+}(PO_4)O_2(OH)_2$, has the same constituents as zairite, $BiFe_3(PO_4)_2(OH)_6$, but this is their only similarity. Zairite is a member of the crandallite group and is isostructural with alunite. The paulkellerite structure is quite different from that of zairite.

EXPERIMENTAL DETAILS

A crystal fragment of paulkellerite chosen from holotype material (NMNS no. 53450) and measuring 0.17 × 0.08 × 0.05 mm was used for the data collection. Intensity data were collected on a fully automated, Nicolet R3m four-circle diffractometer operating at 50 kV and 40v mA with graphite-monochromated Mo$K\alpha$ radiation. A set of 22 reflections was used to center the crystal and subsequently refine the cell dimensions: a = 11.380(3), b = 6.660(3), c = 9.653(3) Å, and β = 115.43(2)°. A unique set of intensity data up to $2\theta = 60°$ was collected in the θ:2θ scanning mode with a scan range of 2° 2θ plus $\alpha_1 - \alpha_2$ separation and scan speeds inversely proportional to intensity, varying from 4 to 29.3°/min. Of the 1086 intensities collected, 858 were considered observed $[I > 3\sigma(I)]$.

Reduction of the intensity data and refinement of the structure were done by the SHELXTL package of programs. Data reduction included background, scaling, Lorentz and polarization, and absorption corrections. For the absorption correction, 11 intense diffraction maxima over the 2θ range of 9 to 60° were chosen for ψ-diffraction-vector scans after the method of North et al. (1968). The ψ-scan set of intensity data was used to refine an ellipsoidal, empirical absorption correction. Absorption correction reduced the merging R of the ψ-scan data set from 15.3% to 3.3%. Considering the high linear-absorption coefficient (μ_l = 525 cm^{-1}), this refinement gives good intensity-data agreement. Scattering curves for neutral atoms from Cromer and Mann (1968) and anomalous dispersion coefficients from Cromer and Liberman (1970) were used in conjunction with a weighting scheme of $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{-1/2}$ with $w = 1$.

CRYSTAL-STRUCTURE ANALYSIS

The mean value of $|E^2 - 1|$ is 0.91 for the region $\sin\theta/\lambda \geq 0.15$, which favors the centrosymmetric space group $C2/c$ for paulkellerite. Phasing of a set of normalized structure factors gave four possible E maps, which were actually two pairs with a shift of origin relating one to the other within a pair. The correct E map was readily determined with the coordinates of the single heavy atom, Bi. The positional and thermal parameters of this general site alone refined to give a residual index R = 20%. From this initial model, a series of refinements, with difference-Fourier maps, showed additional atomic sites. With all the atomic sites accounted for (one Bi, one Fe, one P and four O sites), the model refined to R = 5.4% with isotropic temperature factors.

The final steps of the least-squares refinement involved a conversion to anisotropic temperature factors and the addition of an isotropic primary extinction-correction to the weighting scheme. This resulted in final residual indices of R = 3.4% and R_w = 3.3% using 858 observed reflections to refine the 58 least-squares parameters. At this stage in the crystal-structure refinement, the ΔF synthesis was relatively smooth with only minor differences in electron density associated with the Bi site. This local disturbance is a relatively common feature for crystals with such heavy atoms. The presence of H atoms could not be positively verified.

Table 1 contains the final positional parameters and anisotropic-temperature-factor coefficients; Table 2,[1] the observed and calculated structure factors; and Table 3, the selected interatomic distances and angles.

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[1] A copy of Table 2 may be ordered as Document AM-88-382 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.

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TABLE 1. Positional coordinates and thermal parameters (Å^2) in paulkellerite

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Bi	0.23390(3)	0.03767(6)	0.08772(4)	0.0109(2)	0.0070(2)	0.0118(2)	−0.0002(2)	0.0035(1)	0.0002(2)	0.0104(2)
Fe	½	0	½	0.0095(8)	0.007(1)	0.0115(9)	−0.0010(7)	0.0036(7)	−0.0006(7)	0.0097(7)
P	0	0.1719(6)	¼	0.011(2)	0.004(2)	0.012(2)	0	0.005(1)	0	0.009(1)
O(1)	0.1046(8)	0.0416(13)	0.2386(10)	0.026(4)	0.009(4)	0.017(4)	0.003(3)	0.015(3)	0.001(3)	0.015(3)
O(2)	0.4346(7)	0.1929(13)	0.6078(9)	0.011(3)	0.009(3)	0.017(4)	−0.005(3)	0.003(3)	0.000(3)	0.013(3)
O(3)	0.3512(7)	0.1726(13)	0.9820(9)	0.017(4)	0.011(4)	0.013(4)	0.005(3)	0.008(3)	0.004(3)	0.013(3)
OH	0.3806(7)	0.1410(13)	0.3015(9)	0.012(3)	0.013(4)	0.016(4)	0.000(3)	0.000(3)	−0.004(3)	0.016(3)

Note: Temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \cdots + 2U_{12}hka^*b^*)]$. Esd's are in parentheses.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Although the number and location of the H sites could not be determined from the Fourier synthesis, bond-valence calculations for each oxygen site readily delineated their distribution. These calculations were also useful in determining the valence state of the Fe site. Table 4 gives the individual bond valences and their sums to the various sites based on the constants of Brown (1981) and the bond lengths of Table 3. The bond-valence calculations show that one of the O sites (1.20 v.u.) has a proton associated with it and that the Fe in the Fe site (3.04 v.u.) is in the +3 state, which supports the microchemical test of Dunn et al. (1988). The bond-valence calculations, along with the microchemical tests, give the structural formula $Bi_8Fe_4^{3+}(PO_4)_4O_8(OH)_8$ or simply $Bi_2Fe^{3+}(PO_4)O_2(OH)_2$ with Z = 4. The paulkellerite structure has three different cation polyhedra; P in regular tetrahedral coordination with a mean P–O bond length of 1.528 Å; Fe^{3+} in regular octahedral coordination with a mean Fe–O distance of 2.006 Å; and Bi^{3+} in sevenfold coordination with two long Bi–O distances averaging 3.078 Å and five shorter Bi–O bond lengths averaging 2.325 Å. The Bi polyhedron (Fig. 1) has an approximate square plane of four oxygens (O3, O3, O1, and O2) with an OH apex on one side of this plane and the two more distanct oxygens (O2 and O1) extending in the opposite direction. There is no evidence for a stereochemically active lone pair of electrons associated with the Bi atom, as the most likely site between the distant oxygens has a bond angle of 47°, which does not leave a sufficient volume for such an orbital.

TABLE 3. Selected interatomic distances (Å) and angles (°) in paulkellerite

	P tetrahedron		
P–O(1)	1.515(10) ×2	O(1)–P–O(1)	110.1(7)
P–O(2)	1.540(8) ×2	O(2)–P–O(1)	107.8(4) ×2
Mean	1.528	O(2)–P–O(2)	111.3(5) ×2
		O(2)–P–O(2)	108.4(7)
O(1)–O(1)	2.48(2) ×2	Mean	109.4
O(1)–O(2)	2.47(1) ×2		
O(1)–O(2)	2.52(1) ×2		
Mean	2.49		
	Fe^{3+} octahedron		
Fe–OH	2.041(7) ×2	OH–Fe–O(2)	93.1(3) ×2
Fe–O(2)	1.987(10) ×2	O(2)–Fe–OH	86.9(3) ×2
Fe–O(3)	1.991(9) ×2	O(3)–Fe–OH	90.8(3) ×2
Mean	2.006	O(3)–Fe–O(2)	94.4(4) ×2
		O(3)–Fe–OH	89.2(3) ×2
OH–O(2)	2.77(1) ×2	O(3)–Fe–O(2)	85.6(4) ×2
OH–O(2)	2.92(1) ×2	Mean	90.0
OH–O(3)	2.87(1) ×2		
OH–O(3)	2.83(1) ×2		
O(2)–O(3)	2.70(1) ×2		
O(2)–O(3)	2.92(1) ×2		
Mean	2.84		
	Bi polyhedron (<3.3 Å)		
Bi–O(1)	2.475(12)	O(1)–OH	3.00(1)
Bi–OH	2.136(7)	O(1)–O(3)	3.05(1)
Bi–O(3)	2.192(10)	OH–O(3)	2.96(1)
Bi–O(1)	3.089(9)	OH–O(2)	3.13(1)
Bi–O(2)	3.067(8)	OH–O(3)	3.13(1)
Bi–O(2)	2.690(9)	O(3)–O(1)	3.13(1)
Bi–O(3)	2.134(8)	O(3)–O(2)	2.70(1)
Mean	2.540	O(3)–O(3)	2.68(2)

Note: Esd's are in parentheses.

Paulkellerite has a layered structure parallel to (100) with Bi polyhedral layers alternating with layers of chains (Fig. 2). The single, zig-zag chains consist of alternating, corner-sharing P tetrahedra and Fe octahedra that extend along the **c** axis (Fig. 3). The single chains are not widely separated in the (100) plane because of the interconnecting Bi atoms, each of which bonds to three tetrahedra and three octahedra. In this tight structural configuration there are no OH–O bond lengths less than 3.5 Å for anions not bonded to the same cation, precluding hydrogen bonding.

Paulkellerite has a chemical similarity to zairite, $BiFe(PO_4)_2(OH)_6$, and although the structure of this min-

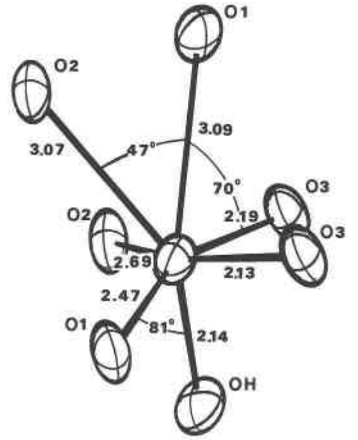

Fig. 1. The Bi coordination polyhedron in paulkellerite.

TABLE 4. Bond-valence sums (v.u.) in paulkellerite

Site	Calc.	Site	Calc.	Site	Sum	Ideal
Bi–O(1)	0.353	P–O(1) ×2	1.339	Bi	2.95	3
Bi–OH	0.738	P–O(2) ×2	1.249	Fe	3.04	3
Bi–O(3)	0.648			P	5.18	5
Bi–O(1)	0.117	Fe–OH ×2	0.458	O(1)	1.81	2
Bi–O(2)	0.121	Fe–O(2) ×2	0.534	O(2)	2.14	2
Bi–O(2)	0.233	Fe–O(3) ×2	0.528	O(3)	1.92	2
Bi–O(3)	0.741			OH	1.20	1

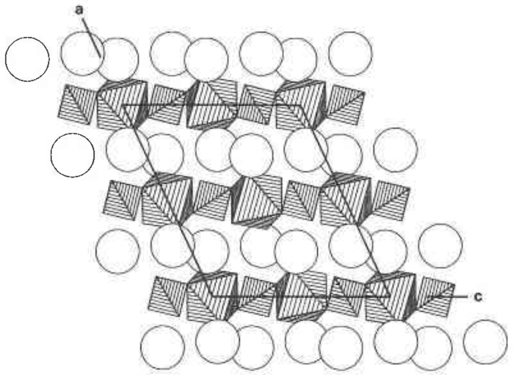

Fig. 2. A projection of the paulkellerite structure on (010). The P tetrahedra and Fe octahedra are ruled, and the Bi atoms are represented by large open circles. (STRUPLO84 plot, Fisher, 1985).

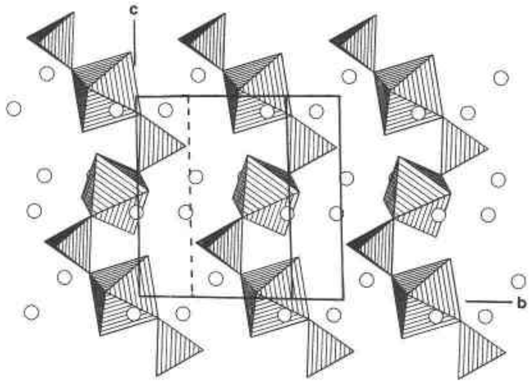

Fig. 3. An inclined **a**-axis projection (**b** axis forward 25°) of the paulkellerite structure. The P tetrahedra (ruled) and Fe octahedra (ruled) join in distinct, single chains. The Bi atoms are represented by small open circles. (STRUPLO84 plot, Fisher, 1985).

eral has not been determined, Van Wambeke (1975) reported that it is a member of the crandallite group. Assuming this is correct, Bi would substitute for Ca and Fe for Al in the crandallite structure (Blount, 1974). The dominant topological features would be sheets of Fe octahedra interlayered with sheets of Bi twelvefold coordination polyhedra and P tetrahedra. This structure differs greatly from paulkellerite with tetrahedral-octahedral single chains tightly linked by sevenfold coordinated Bi. The paulkellerite structure is unique.

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