

The Crystal Structure of Orthorhombic Barium Dihydrogenphosphate

BY B. PRELESNIK, R. HERAK AND M. ČURIĆ

Laboratory of Solid State Physics, 'Boris Kidrič' Institute, Beograd, PO Box 522, Yugoslavia

AND I. KRSTANOVIĆ

Faculty of Mining, Geology and Metallurgy, University of Beograd, Beograd, Yugoslavia

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The structure of the orthorhombic phase of barium dihydrogenphosphate was determined from 1253 independent data collected on an automatic diffractometer. The crystals are orthorhombic, space group *Pccn*, $a = 10.242$ (3), $b = 7.793$ (5), $c = 8.560$ (4) Å, $Z = 4$. The structure was solved by the heavy-atom method and refined by least squares to a final R value of 0.031. The crystal structure consists of PO_4 tetrahedra, forming sheets parallel to the yz crystallographic plane, and Ba ions. Within the sheets the PO_4 tetrahedra are joined together by strong hydrogen bonds of 2.57 and 2.60 Å. The distortion indices $\text{DI}(\text{TO})$, $\text{DI}(\text{OTO})$, $\text{DI}(\text{OO})$ and the bond-length–bond-strength relationships are calculated and discussed.

Introduction

At room temperature and atmospheric pressure crystals of $\text{Ba}(\text{H}_2\text{PO}_4)_2$ can exist in two different forms, triclinic and orthorhombic. During growth from solution both forms are present in approximately equal amounts. In time the proportion of orthorhombic crystals increases, and the triclinic form eventually vanishes. The crystal structure of the triclinic phase has already been studied (Herak & Krstanović, 1975), but a final refinement with anisotropic temperature factors is now in progress and the dielectric anomalies of the compound have been described (Živanović & Huter, 1976). The aim of the present study was to determine the crystal structure of the orthorhombic phase.

Experimental

The crystal data are: barium dihydrogenphosphate, $M_r = 331.46$, $a = 10.242$ (3), $b = 7.793$ (5), $c = 8.560$ (4) Å, $U = 683.2$ Å³; $D_m = 3.19$ (pycnometric), $Z = 4$, $D_x = 3.22$ g cm⁻³, space group *Pccn*; Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 20.17$ cm⁻¹.

The unit-cell parameters were initially determined from oscillation and Weissenberg single-crystal photographs and then adjusted by least-squares refinement of the setting angles of 15 strong reflexions which had been centred on a Syntex PI diffractometer (using Mo $K\alpha$ radiation).

Intensity data of 1253 reflexions were collected by the θ - 2θ scan technique, with a 2° min⁻¹ scan speed and Mo $K\alpha$ (Zr-filtered) radiation, for 30 s on each side of the peak. The constancy of a standard reflexion showed that the crystal did not change. No absorption correction was made, the radius of the spherical crystal being 0.22 mm.

Structure determination

As $Z = 4$, the Ba atom was expected to lie in a special position. When the structure was solved by the heavy-atom method, this atom was found to be on a twofold axis. The two H atoms were found by a 'difference' synthesis. In the final stage of full-matrix least-squares refinement, all atoms, except H, were given anisotropic vibrational parameters. The function minimized in the refinement after introduction of extinction was $\sum w\{F_o - |F_c/(1 + gD)|\}^2$, where g is the extinction coefficient, I is the uncorrected intensity of a reflexion, and $w = 1$. The analysis converged at $R = 0.031$ with $g = 11 \times 10^{-7}$.*

The final atomic coordinates with their standard deviations are given in Table 1. The atomic scattering factors used, including $\Delta f'$ and $\Delta f''$ for Ba, were taken from *International Tables for X-ray Crystallography* (1962).

Discussion

The crystal structure of barium dihydrogenphosphate consists of PO_4 tetrahedra, forming sheets parallel to the yz crystallographic plane, with abscissae of x and $\frac{1}{2} + x$, and Ba ions (Fig. 1). The Ba polyhedron is irregular and consists of eight O atoms belonging to six PO_4 groups. The strong hydrogen bonds of 2.573 and 2.605 Å act between PO_4 groups within the same sheet. O(1), engaged in chains, is not involved in hydrogen-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32981 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

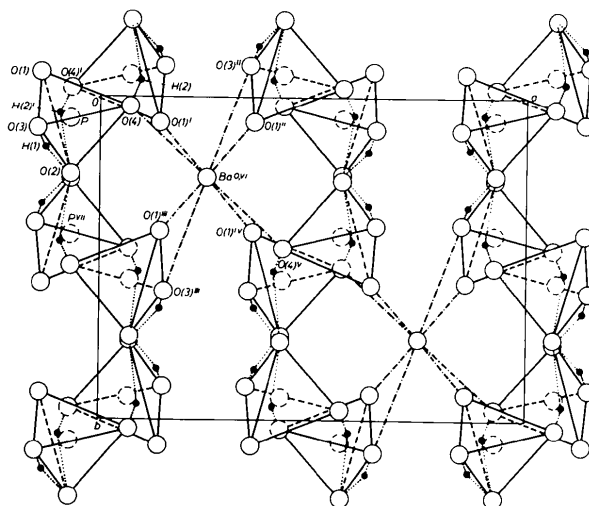
Table 1. *Final positional parameters*

Standard deviations are given in parentheses.

	x	y'	z
Ba	0.2500 (0)	0.2500 (0)	0.09482 (3)
P	-0.0755 (3)	0.0717 (1)	0.2104 (1)
O(1)	-0.1414 (3)	-0.0807 (1)	0.1408 (4)
O(2)	-0.0714 (4)	0.2357 (4)	0.1194 (4)
O(3)	-0.1456 (4)	0.0944 (4)	0.3728 (4)
O(4)	0.0718 (3)	0.0323 (4)	0.2485 (4)
H(1)	-0.128 (6)	0.161 (9)	0.419 (7)
H(2)	0.100 (7)	-0.060 (10)	0.280 (10)

bond formation. O(2), not being in the coordination sphere of the Ba atom, acts as an acceptor of two hydrogen bonds, and O(3) and O(4) are hydrogen-bond donors.

From Table 2(b) it could be concluded that the longest distances in the PO₄ group are those between the P and O atoms with covalently bonded H atoms

Fig. 1. A view of the structure down the *c* axis.Table 2. *Bond lengths (Å) and interbond angles (°) with standard deviations in parentheses*

(a) Barium coordination polyhedron

Ba—O(1) ^{i,iv}	2.654 (3)	Ba—O(3) ^{ii,iii}	2.902 (3)	Ba—O(4) ^{0,v}	2.818 (3)
Ba—O(1) ^{ii,iii}	2.846 (3)				
O(1) ⁱⁱ —Ba—O(1) ⁱⁱⁱ	74.6 (1)	O(1) ^{iii,ii} —Ba—O(4) ^{0,v}	66.6 (1)	O(1) ^{iv,i} —Ba—O(4) ^{v,0}	77.5 (1)
O(1) ⁱ —Ba—O(1) ^{iv}	81.1 (1)	O(1) ^{iii,ii} —Ba—O(4) ^{v,0}	69.8 (1)	O(3) ⁱⁱ —Ba—O(3) ⁱⁱⁱ	169.0 (1)
O(1) ^{ii,iii} —Ba—O(1) ^{iv}	122.5 (1)	O(1) ^{iv,i} —Ba—O(3) ^{ii,iii}	112.2 (1)	O(3) ^{ii,iii} —Ba—O(4) ^{0,v}	68.7 (1)
O(1) ^{iii,ii} —Ba—O(1) ^{iv}	132.1 (1)	O(1) ^{iv,i} —Ba—O(3) ^{ii,iii}	76.5 (1)	O(3) ^{ii,iii} —Ba—O(4) ^{v,0}	105.9 (1)
O(1) ^{iii,ii} —Ba—O(3) ^{ii,iii}	49.6 (1)	O(1) ^{iv,i} —Ba—O(4) ^{0,v}	157.7 (1)	O(4) ⁰ —Ba—O(4) ^v	124.3 (1)
O(1) ^{iii,ii} —Ba—O(3) ^{ii,iii}	119.8 (1)				

(b) PO₄ tetrahedron

P—O(1)	1.491 (3)	P—O(3)	1.575 (3)	P—O(4)	1.573 (3)
P—O(2)	1.498 (3)				
O(1)—P—O(2)	119.0 (2)	O(1)—P—O(4)	111.2 (2)	O(2)—P—O(4)	104.3 (2)
O(1)—P—O(3)	103.6 (2)	O(2)—P—O(3)	112.1 (2)	O(3)—P—O(4)	106.0 (2)

(c) Atoms involved in the hydrogen bonding

H(1)—O(3)	0.67 (7) }				
H(1)···O(2)	1.98 (6) }	O(3)—H(1)···O(2) ^{vi}	151 (7)	O(3)···O(2) ⁱⁱ	2.605 (5)
H(2)—O(4)	0.81 (8) }				
H(2)···O(2)	1.84 (9) }	O(4) ⁱ —H(2) ^j ···O(2)	146 (8)	O(4) ⁱ ···O(2)	2.573 (4)

(d) Some angles about O atoms

Ba—O(1) ^{iii,ii} —P ^{iii,ii}	103.2 (1)	Ba ^{vi} —O(1) ^{iii,ii} —P ^{iii,ii}	152.8 (1)
Ba—O(3) ^{iii,ii} —P ^{iii,ii}	98.6 (2)	Ba—O(4) ^{0,v} —P ^{0,v}	114.0 (2)
P—O(3)—H(1)	120 (5)	P—O(4)—H(2)	126 (6)
Ba—O(1)—Ba ^{vi}	120.15 (a)		

Symmetry code

None or 0	x, y, z	(iv)	$\frac{1}{2} + x, \frac{1}{2} + y, \bar{z}$
(i)	$\bar{x}, \bar{y}, \bar{z}$	(v)	$\frac{1}{2} - x, \frac{1}{2} - y, z$
(ii)	$\frac{1}{2} + x, y, \frac{1}{2} - z$	(vi)	$\frac{1}{2} - x, y, \frac{1}{2} + z$
(iii)	$-x, \frac{1}{2} + y, \frac{1}{2} - z$	(vii)	$x, \frac{1}{2} - y, \frac{1}{2} + z - 1$

Table 3. *Individual and combined bond strengths of the atoms in the structure*

	O(1)	O(2)	O(3)	O(4)	s_i
Ba	0.587 (0.223 + 0.364)	—	0.195	0.239	2.042*
P	1.435	1.403	1.134	1.141	5.113
H(1)	—	0.299	0.701	—	1.000
H(2)	—	0.329	—	0.671	1.000
s_i	2.022	2.031	2.030	2.051	—

* Values should be doubled when $\sum s_i$ is calculated for Ba.

and, consequently, the angle O(3)–P–O(4) is small. On the other hand, P–O(1) and P–O(2) are the shortest distances in the PO₄ group and the O(1)–P–O(2) angle is large. Since the O(1)–O(3) edge is common to the Ba and P polyhedra, the O(1)–P–O(3) angle is, in accordance with Pauling's (1960) rule, the smallest angle in the tetrahedron. A similar situation was found in the crystal structure of Ca(H₂PO₄)₂ (Dickens *et al.*, 1973).

The mean values of the P–O bond lengths and O–P–O valence angles (1.536 Å and 109.4°) are the same as those found in the study of the shapes of 31 acidic phosphates (Baur, 1974). The three distortion indices defining the deviation from the tetrahedron, DI(TO), DI(OTO) and DI(OO), are 0.026, 0.043 and 0.022 respectively for Ba(H₂PO₄)₂. DI(OTO) and DI(OO) are outside the range of the corresponding mean values of 0.018, 0.026 and 0.012 reported by Baur (1974).

Table 3 gives the bond-length–bond-strength relationships as calculated by universal curves, $s =$

$(R/R_0)^{-1}$ (Brown & Shannon, 1973; Brown & Wu, 1976). As the positions of the H atoms in the crystal structure were determined with low precision, the valence–bond-length correlations for O–H and H...O were calculated by the use of s versus O...O curves valid for weak hydrogen bonds. Nevertheless, taking $s_{\text{acceptor}} = 1 - s_{\text{donor}}$, correlations seem applicable for Ba(H₂PO₄)₂.

It was stated (Brown & Wu, 1976) that Ba frequently gives a poor $\sum s_i$, but with the values $R_1 = 2.297$ and $N = 7.00$, as represented by the same authors, 2.042 valence units were obtained for this atom.

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