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Crystal Structure of Bismuth Polyphosphate, $[Bi(PO_3)_3]_x$

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$[Bi(PO_3)_3]_x$ crystallizes in space group $P2_1/a$ with $a=13{\cdot}732$ Å, $b=6{\cdot}933$ Å, $c=7{\cdot}152$ Å, $\beta=93{\cdot}35°$, $Z=4$. The crystals are twinned. The anion consists of infinite spiral-like chains of PO_4 tetrahedra with six tetrahedra per turn. Bi is coordinated by seven oxygen atoms, six of which have distances between 2·20 and 2·43 Å to Bi; one has a distance of 2·79 Å.

Introduction

As a part of an investigation of compounds in the system Bi_2O_3–P_2O_5–H_2O the crystal structure of $Bi(PO_3)_3$ was determined. According to its chemical behaviour this compound should be a linear polyphosphate, $[Bi(PO_3)_3]_x$. It was prepared by Tschudinowa, Lawrow & Tananajew (1972).

Crystal data

Bismuth polyphosphate forms colourless, column-like crystals with approximately square cross section, which split easily parallel to the column axis (y axis). The side faces of the columns are (100) and (001).

The unit-cell dimensions were determined by Guinier photographs (Cu $K\alpha$, $\lambda=1{\cdot}5418$ Å) and single-crystal measurements on the diffractometer (Mo $K\alpha$, $\lambda=0{\cdot}71069$ Å), the symmetry of intensities and the systematic extinctions by oscillation, Weissenberg and precession photographs. The results are given in Table 1.

Table 1. *Crystal data*

$a=13{\cdot}732\pm0{\cdot}002$, $b=6{\cdot}933\pm0{\cdot}001$, $c=7{\cdot}152\pm0{\cdot}001$ Å
$\beta=93{\cdot}35°\pm0{\cdot}01°$ (all at 20 °C)
$V=679{\cdot}7$ Å^3 $Z=4$ $Bi(PO_3)_3$
$D_m=4{\cdot}38$ $D_x=4{\cdot}36$ g cm^{-3}
Laue class: $2/m$
Space group: $P2_1/a=C_{2h}^5$.

Bismuth polyphosphate crystals are always twinned; [010] is the twin axis. Twinning seems to be the consequence of a displacive transformation by which the modification under consideration is formed from a high-temperature modification of orthorhombic symmetry. As expected in such a case, the intensities of equivalent reflexions in the two orientations are the same. Nethertheless occasionally crystals can be found in which these intensities are different. Differential thermal analysis shows at 690 °C (on heating at 4 °C/min, 670 °C on cooling) a reversible effect which confirms the above-mentioned theory of twinning.

Measurement of intensities

Intensity data were collected on a Hilger four-circle diffractometer with a crystal shaped like an orthogonal prism of dimensions $0{\cdot}068\times0{\cdot}068\times0{\cdot}150$ mm. Intensities were measured and corrected under the following conditions:

Radiation was Mo $K\alpha$, selected by a graphite monochromator; integrated intensities for reflexions with $0\leq5°$ by ω scan, otherwise by $\omega/2\theta$ scan; correction for p, L and absorption; range: $hk0$–$hk8$ up to $\sin\theta/\lambda=0{\cdot}703$, which gives 1912 reflexions unrelated by symmetry of which 1584 were observed.

Twinning of the crystals only scarcely disturbs the collection of intensity data, because only in the layers $hk0$, $hk9$ ... are the reflexions of both the orientations unresolved. For this reason the ninth layer has not been measured. The intensities in the layer $hk0$ were scaled by a factor which was calculated from a set of reflexions for which the corrected intensities for both the orientations had been determined. In the layers $hk4$ and $hk5$ reflexions for the two orientations are in approximately the same position and therefore whether the resolution was good enough was tested; this was found to be so.

Structure determination

The approximate structure was determined by the heavy-atom method and refined in several least-squares cycles. In the form factor of bismuth the correction terms $\Delta f'$ and $\Delta f''$ (*International Tables for X-ray Crystallography*, 1962) were taken into account. The final R index, calculated with 1890 reflexions is $R=0{\cdot}046$. For $|F_o|/F_c$ values and parameters see Tables 2–4.

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Results

The anion

Crystal structure analysis has verified the result of the chemical investigations, that the compound under consideration is polyphosphate. The PO_4 tetrahedra are connected *via* corners to infinite spiral-like chains, running through the crystal parallel to the y axis.

There are six tetrahedra per turn of the spiral, which means the chains are '6er Ketten' (Fig. 1). The pitch

Table 2. *Structure factors*

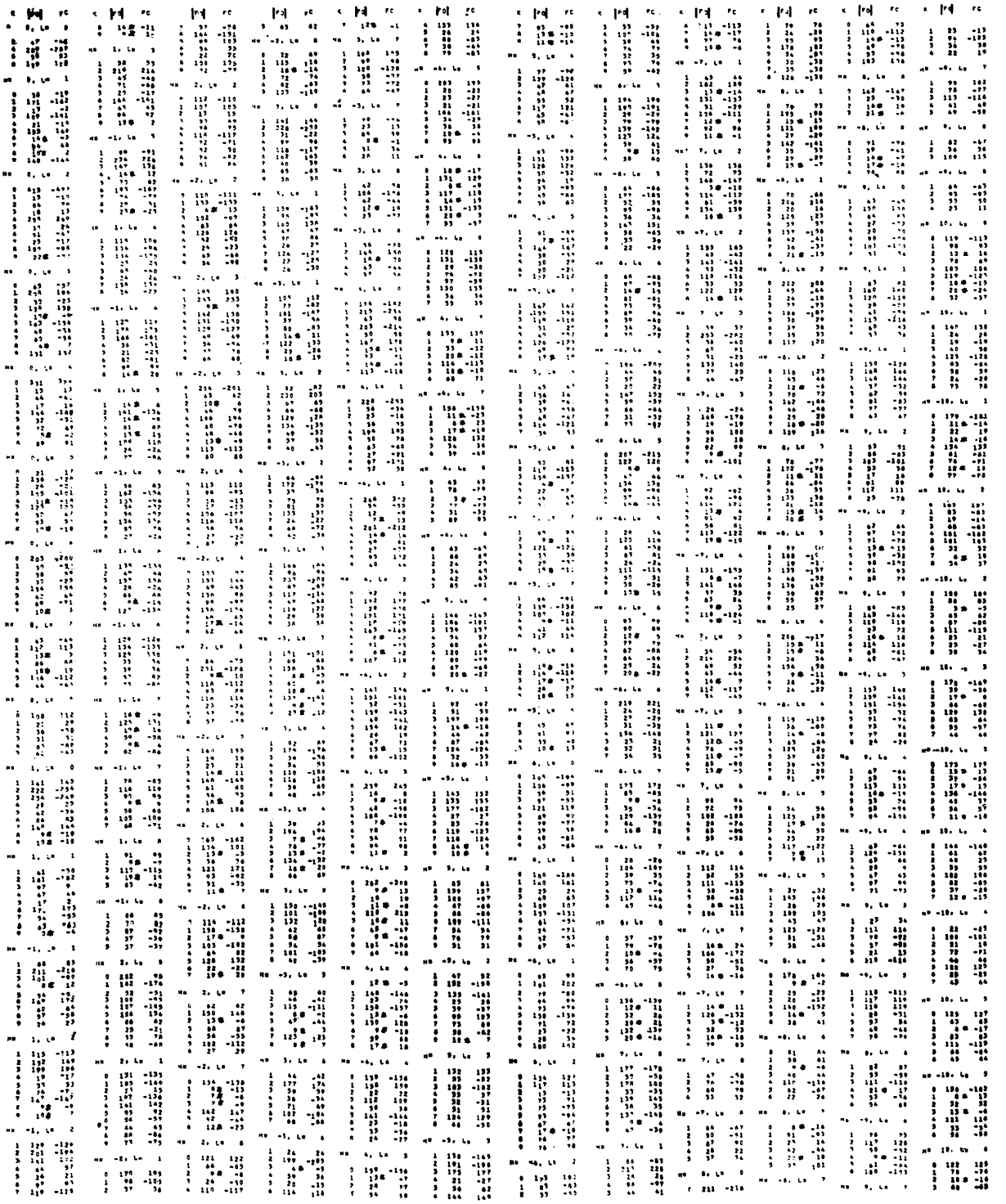


Table 2 (*cont.*)

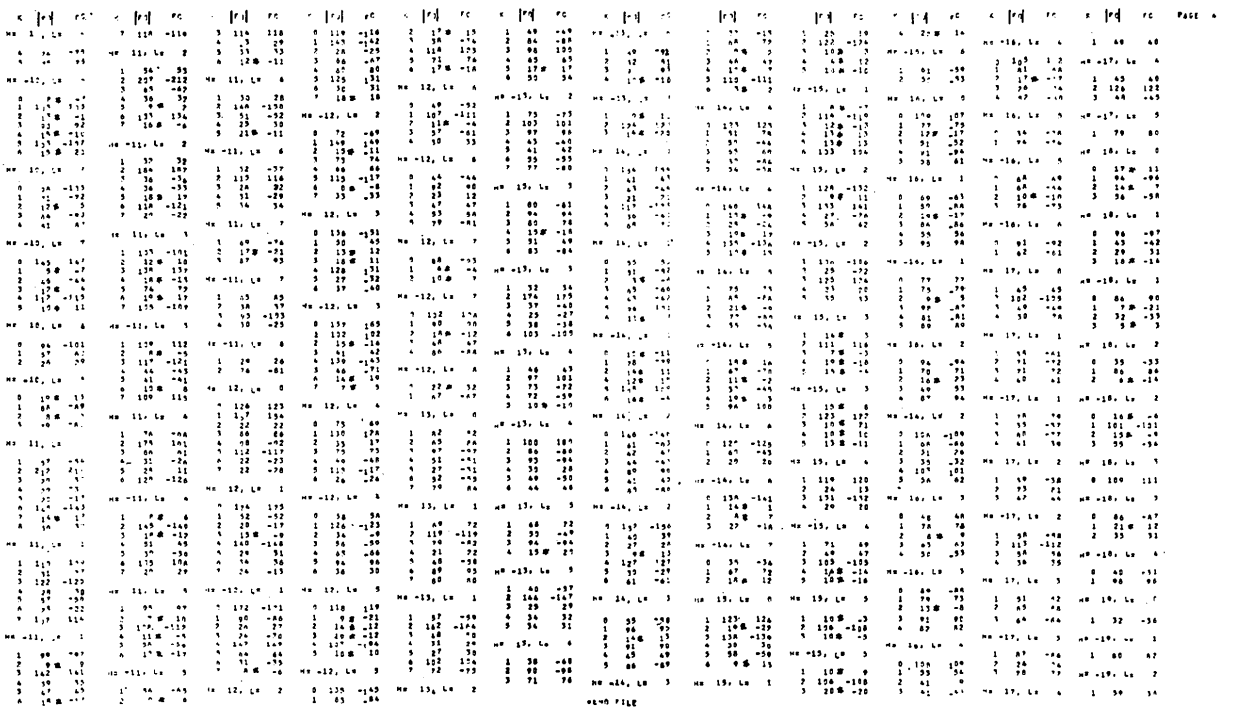


Table 3. *Atomic coordinates*

In brackets: $10^4 \times \sigma$.

	x	*y*	*z*
Bi	0·0680 (0)	0·1363 (1)	0·2425 (1)
P(1)	0·3235 (2)	0·1006 (5)	0·2934 (5)
P(2)	0·3419 (2)	0·1060 (5)	0·7066 (4)
P(3)	0·1365 (2)	0·1848 (5)	0·7680 (4)
O(1)	0·2257 (6)	0·1747 (14)	0·2198 (14)
O(2)	0·2408 (6)	0·0847 (14)	0·8035 (13)
O(3)	0·4089 (7)	0·2295 (15)	0·2798 (16)
O(4)	0·3110 (7)	0·0276 (15)	0·5011 (12)
O(5)	0·1566 (7)	0·4033 (13)	0·8153 (13)
O(6)	0·3696 (7)	0·3110 (14)	0·7044 (16)
O(7)	0·0910 (7)	0·4602 (14)	0·2030 (14)
O(8)	0·0743 (6)	0·1104 (14)	0·9176 (11)
O(9)	0·0959 (7)	0·1563 (16)	0·5701 (11)

of the spiral is *b*. Every third tetrahedron is in nearly the same position along the chain (similar *y* coordinates of the P atoms). The groups of three thus formed are connected to one another by a steep step [O(5) to O(5′)].

Distances and angles have the values usually found in polyphosphates (Tables 5 and 6).

The cation

The coordination polyhedron of bismuth is formed by seven terminal oxygen atoms. One of these (at a distance of 2·79 Å) is much further from the bismuth atom than the other six (Fig. 2). The shape of the coordination polyhedron is irregular.

The coordination polyhedra form pairs with a com-

Table 4. *Thermal parameters*

$B_{11} = 10^4 \cdot 2\pi^2 a^{*2} U_{11}, \ldots$. In brackets: standard deviations.

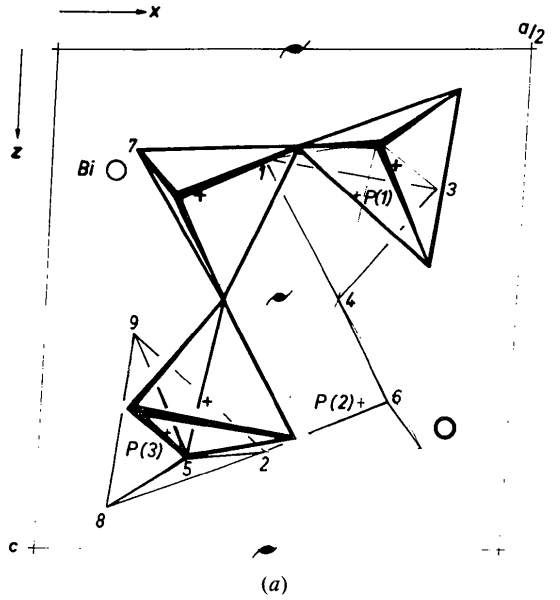
	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Bi	7 (0)	30 (1)	18 (1)	−2 (2)	−2 (0)	1 (1)
P(1)	8 (1)	34 (7)	40 (6)	−7 (9)	−2 (4)	0 (5)
P(2)	9 (1)	25 (6)	33 (6)	−5 (9)	−5 (4)	3 (5)
P(3)	9 (1)	34 (6)	19 (6)	−3 (9)	−1 (4)	−3 (4)
O(1)	7 (4)	64 (22)	95 (20)	1 (32)	−8 (14)	8 (14)
O(2)	8 (4)	53 (19)	52 (18)	22 (28)	−3 (13)	12 (14)
O(3)	13 (5)	63 (20)	106 (22)	−16 (34)	22 (16)	−23 (16)
O(4)	25 (5)	69 (20)	8 (16)	30 (28)	−3 (14)	−9 (17)
O(5)	23 (5)	12 (18)	54 (18)	12 (27)	14 (14)	−12 (14)
O(6)	18 (5)	37 (19)	127 (23)	−19 (32)	−7 (16)	−16 (15)
O(7)	13 (5)	45 (20)	103 (21)	0 (32)	−11 (14)	−25 (15)
O(8)	6 (4)	66 (20)	10 (14)	−9 (28)	2 (11)	−11 (15)
O(9)	27 (5)	96 (22)	18 (14)	−42 (31)	−8 (12)	0 (19)

Table 5. *Phosphorus–oxygen distances*

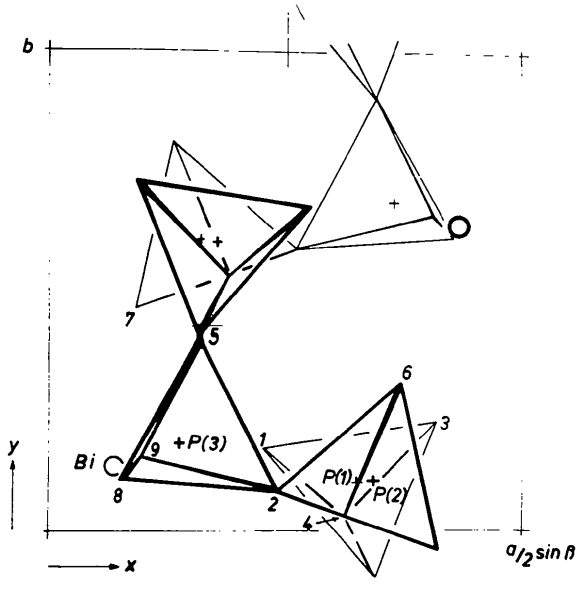
b = Oxygen in a P–O–P bridge.

P(1)–O(1)	1·505 ± 0·010 Å	P(3)–O(2)*b*	1·597 ± 0·009 Å
O(3)	1·482 ± 0·010	O(5)*b*	1·573 ± 0·009
O(4)*b*	1·587 ± 0·009	O(8)	1·499 ± 0·009
O(5′)*b*	1·605 ± 0·009	O(9)	1·503 ± 0·009

P(2)–O(2)*b*	1·594 ± 0·009 Å
O(4)*b*	1·601 ± 0·009
O(6)	1·472 ± 0·010
O(7′)	1·490 ± 0·010



(*a*)



(*b*)

Fig. 1. The polyphosphate chain. (*a*) Projection down the chain. (*b*) Projection on the chain (along *z*).

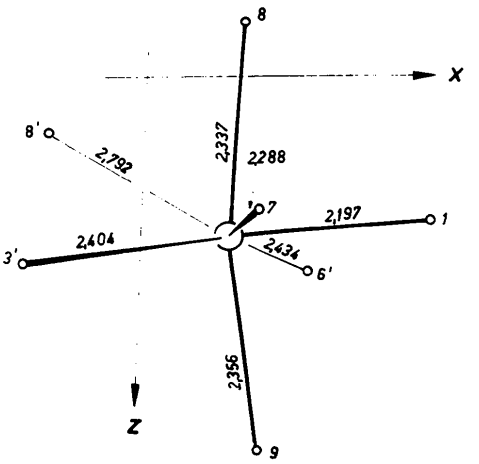


Fig. 2. Distances in the coordination polyhedron of bismuth. Standard deviation ≤0·010 Å.

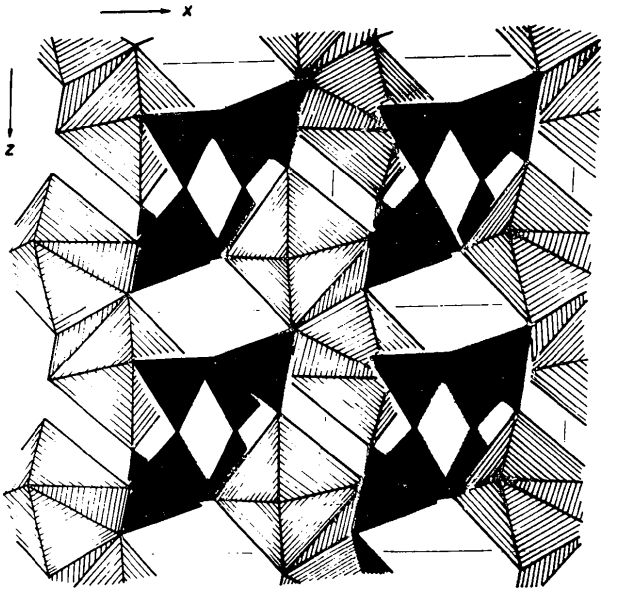


Fig. 3. *xz* projection of the structure. Reduced in scale compared with Figs. 1 and 2. Black: PO_4 tetrahedra. Hatched: coordination polyhedra of Bi.

Table 6. *Valence angles in the polyphosphate chain*

b = Oxygen in a P–O–P bridge.

O(1)—P(1)–O(3)		117·7 (6)°	O(2)*b*–P(3)—O(5)*b*		103·9 (5)°
O(1)	O(4)*b*	107·0 (5)	O(2)*b*	O(8)	106·2 (5)
O(1)	O(5′)*b*	107·2 (5)	O(2)*b*	O(9)	111·9 (5)
O(3)	O(4)*b*	112·5 (6)	O(5)*b*	O(8)	106·1 (5)
O(3)	O(5′)*b*	108·9 (6)	O(5)*b*	O(9)	112·3 (5)
O(4)*b*	O(5′)*b*	102·3 (5)	O(8)	O(9)	115·5 (5)
O(2)*b*–P(2)–O(4)*b*		100·2 (5)	P(1)—O(4)*b*–P(2)		135·5 (7)
O(2)*b*	O(6)	109·1 (6)	P(2)—O(2)*b*–P(3)		133·3 (6)
O(2)*b*	O(7′)	106·3 (5)	P(3)—O(5)*b*–P(1′)		138·5 (6)
O(4)*b*	O(6)	111·8 (6)			
O(4)*b*	O(7′)	107·0 (5)			
O(6)	O(7′)	120·4 (6)			

mon edge and these double polyhedra are isolated in space from one another, which means that they have no Bi–O–Bi contacts. The distance between the Bi atoms within a double polyhedron is 4·28 Å and of the other Bi–Bi distances 4·64 Å is the shortest one, all the others being longer than 6·5 Å.

The overall structure

Fig. 3 shows a projection of the structure. Every double polyhedron connects four polyphosphate chains and conversely every chain four rows of double polyhedra.

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Crystal Structure of the Polyphosphate $[BiH(PO_3)_4]_x$

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$[BiH(PO_3)_4]_x$ forms triclinic crystals, space group $P\bar{1}$, with unit-cell dimensions $a=8{\cdot}625$, $b=8{\cdot}866$, $c=7{\cdot}062$ Å, $\alpha=112{\cdot}17°$, $\beta=108{\cdot}54°$, $\gamma=98{\cdot}49°$. In the anion PO_4 tetrahedra are connected *via* corners to infinite chains. The identity period in the chains is the lattice constant c and four tetrahedra form the motif. Bi is surrounded by seven oxygen atoms at distances ranging from 2·27 to 2·55 Å. The shape of the coordination polyhedron is irregular. The position of the hydrogen atom was determined with high probability from a difference map.

Introduction

In the course of investigations of the crystal chemistry of condensed bismuth phosphate the crystal structure of a compound of composition $BiH(PO_3)_4$ was determined. In paper chromatography this compound, which was synthesized by Tschudinowa, Lawrow & Tananajew (1972), behaves like a linear polyphosphate. Proton resonance absorption shows the substance to contain chemically bound water (Grimmer & Tschudinowa, 1972). This confirms the above-mentioned result.

Crystal data

Crystals of $BiH(PO_3)_4$ are colourless and have the shape of columns (axis parallel to z) with a rectangular cross section. Mechanical stress causes the crystals to split into fibres parallel to the column axis. The dimensions of the reduced cell, determined from measurements with Mo $K\alpha$ radiation ($\lambda=0{,}71069$ Å) on a diffractometer, and some other crystal data are collected in Table 1.

Table 1. *Crystal data*

$a=8{\cdot}625\pm0{\cdot}001$, $b=8{\cdot}866\pm0{\cdot}001$, $c=7{\cdot}062\pm0{\cdot}001$ Å
$\alpha=112{\cdot}17\pm0{\cdot}01°$, $\beta=108{\cdot}54\pm0{\cdot}01°$, $\gamma=98{\cdot}49\pm0{\cdot}01°$
(values at 20 °C)
$V=451{\cdot}47$ Å^3 $Z=2BiH(PO_3)_4$
$D_m=3{\cdot}86$ $D_x=3{\cdot}87$ g cm^{-3}
Laue class: $\bar{1}$
Space group: $P\bar{1}$ (from the structure analysis)

Intensity data and structure determination

The intensity data were collected as described in Table 2. In structure determination 2432 crystallographically independent reflexions were used of which 2256 were observed.

The structure was determined by the heavy-atom method. The final R value, calculated with 2390 reflexions, after three isotropic and two anisotropic

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