

K₂Ho(PO₄)(WO₄)

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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{W}-\text{O}) = 0.004$ Å; R factor = 0.029; wR factor = 0.071; data-to-parameter ratio = 25.2.

A new compound, dipotassium holmium(III) phosphate(V) tungstate(VI), K₂Ho(PO₄)(WO₄), has been obtained during investigation of the K₂O–P₂O₅–WO₃–HoF₃ phase system using the flux technique. The compound is isotypic with K₂Bi(PO₄)(WO₄). Its framework structure consists of flat $\infty^2[\text{HoPO}_4]$ layers parallel to (100) that are made up of $\infty^1[\text{HoO}_8]$ zigzag chains interlinked *via* slightly distorted PO₄ tetrahedra. WO₄ tetrahedra are attached above and below these layers, leaving space for the K⁺ counter-cations. The HoO₈, PO₄ and WO₄ units exhibit 2 symmetry.

Related literature

For related structures, see: Ben Amara & Dabbabi (1987); Marsh (1987); Zatovsky, Terebilenko, Slobodyanik & Baumer (2006); Zatovsky, Terebilenko, Slobodyanik, Baumer & Shishkin (2006).

Experimental

Crystal data

K ₂ Ho(PO ₄)(WO ₄)	$V = 1646.6$ (4) Å ³
$M_r = 585.95$	$Z = 8$
Orthorhombic, <i>Ibca</i>	Mo $K\alpha$ radiation
$a = 6.8820$ (10) Å	$\mu = 24.72$ mm ⁻¹
$b = 12.1485$ (18) Å	$T = 293$ (2) K
$c = 19.695$ (3) Å	$0.10 \times 0.09 \times 0.07$ mm

Data collection

Oxford Diffraction Xcalibur-3 CCD diffractometer
Absorption correction: multi-scan based on the method by Blessing (1995)
 $T_{\min} = 0.102$, $T_{\max} = 0.177$
8608 measured reflections
1561 independent reflections
1257 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.055$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.071$
 $S = 1.15$
1561 reflections
62 parameters
 $\Delta\rho_{\max} = 1.90$ e Å⁻³
 $\Delta\rho_{\min} = -1.73$ e Å⁻³

Table 1

Selected bond lengths (Å).

W1—O2	1.749 (4)	Ho1—O3 ⁱⁱ	2.401 (3)
W1—O1	1.788 (3)	Ho1—O4	2.428 (3)
Ho1—O4 ⁱ	2.274 (3)	P1—O3	1.525 (3)
Ho1—O1	2.342 (3)	P1—O4	1.552 (3)

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $x, y + \frac{1}{2}, -z + 1$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2196).

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supplementary materials

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K₂Ho(PO₄)(WO₄)

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Comment

The co-existence of different anionic units in crystal structures represents an interesting field of investigation. One of the first structural examples of a combination of PO₄ with MoO₄/WO₄ tetrahedra, *viz.* Na₂Y(MoO₄)(PO₄), was reported to be monoclinic with space group *C2/c* (Ben Amara & Dabbabi, 1987). Later this structure was reinvestigated and described as orthorhombic, space group *Ibca* (Marsh, 1987). Recently, the compounds K₂Bi(PO₄)(MO₄) (*M*=Mo, W) with isotypic structures were obtained by application of the flux method (Zatovsky, Terebilenko, Slobodyanik & Baumer, 2006; Zatovsky, Terebilenko, Slobodyanik, Baumer & Shishkin, 2006). Herein, we report the flux synthesis and crystal structure of a new member of the *A₂B(PO₄)(AO₄)* (*A* = Na, K; *B* = lanthanide, Y, Bi; *M* = Mo, W) family.

One of the characteristic features of this structure type is the "segregation" of slightly distorted PO₄ and WO₄ tetrahedra into adjacent layers (Fig. 1). The first layer with composition ²_∞[HoPO₄] contains ¹_∞[HoO₈] zigzag chains (Fig. 2). The connection between neighboring chains is achieved *via* PO₄ tetrahedra. On the top and on the bottom of the ²_∞[HoPO₄] layer, WO₄ tetrahedra are attached. All [HoO₈], PO₄ and WO₄ units exhibit 2 symmetry with bond lengths in the typical ranges (Table 1). The K⁺ cations are situated in the resulting interlayer space and are surrounded by 8 oxygen atoms with K—O bond lengths ranging from 2.683 (4) Å to 3.133 (4) Å.

Experimental

Single crystals of the title compound were grown from a multicomponent high-temperature solution. A mixture of 4.645 g K₂W₂O₇, 0.865 g KPO₃, and 1.150 g K₄P₂O₇ was heated in a platinum crucible up to 1173 K which is above the melting temperature. Then 0.200 g of HoF₃ were added to this melt under stirring. The final mixture was held at this temperature for 1 h and cooled down to room temperature with a rate of 30 K h⁻¹. The solidified melt was leached out with warm water to dissolve the superfluous flux. The final product consisted of beige needle-like crystals with a maximum length of up to 5 mm.

Refinement

The highest peak and the deepest hole of the final Fourier map are located 0.58 Å from atom W1 and 1.11 Å from the same atom, respectively.

Figures

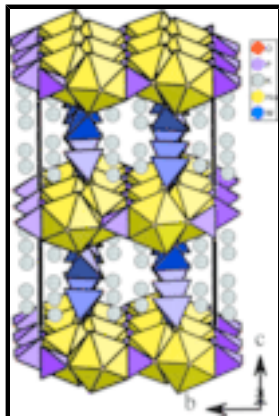


Fig. 1. The layered structure of $K_2Ho(PO_4)(WO_4)$, leaving space where the K^+ ions are located.

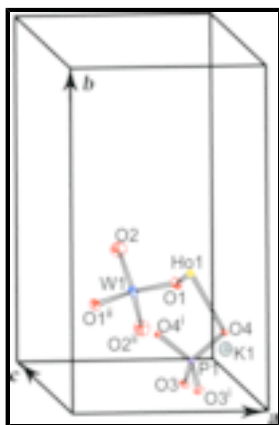


Fig. 2. View of $K_2Ho(PO_4)(WO_4)$ with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $1,5-x; y; 1-z$; (ii) $1-x; 0.5-y; z$].

Dipotassium holmium(III) phosphate(V) tungstate(VI)

Crystal data

$K_2Ho(PO_4)(WO_4)$

$M_r = 585.95$

Orthorhombic, *Ibca*

Hall symbol: $-I\ 2b\ 2c$

$a = 6.8820(10)\ \text{\AA}$

$b = 12.1485(18)\ \text{\AA}$

$c = 19.695(3)\ \text{\AA}$

$V = 1646.6(4)\ \text{\AA}^3$

$Z = 8$

$F_{000} = 2064$

$D_x = 4.727\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 8608 reflections

$\theta = 3.4\text{--}33.0^\circ$

$\mu = 24.72\ \text{mm}^{-1}$

$T = 293(2)\ \text{K}$

Prism, pale beige

$0.10 \times 0.09 \times 0.07\ \text{mm}$

Data collection

Oxford Diffraction XCalibur-3 CCD
diffractometer

Radiation source: fine-focus sealed tube

1561 independent reflections

1257 reflections with $I > 2\sigma(I)$

Monochromator: graphite $R_{\text{int}} = 0.055$
 $T = 293(2)$ K $\theta_{\text{max}} = 33.0^\circ$
 φ and ω scans $\theta_{\text{min}} = 3.4^\circ$
 Absorption correction: multi-scan based on the method by Blessing (1995) $h = -10 \rightarrow 10$
 $T_{\text{min}} = 0.102$, $T_{\text{max}} = 0.177$ $k = -18 \rightarrow 18$
 8608 measured reflections $l = -30 \rightarrow 29$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 3.2575P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 Least-squares matrix: full $(\Delta/\sigma)_{\text{max}} < 0.001$
 $R[F^2 > 2\sigma(F^2)] = 0.029$ $\Delta\rho_{\text{max}} = 1.90 \text{ e } \text{Å}^{-3}$
 $wR(F^2) = 0.071$ $\Delta\rho_{\text{min}} = -1.73 \text{ e } \text{Å}^{-3}$
 $S = 1.15$ Extinction correction: SHELXL97 (Sheldrick, 2008),
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 1561 reflections Extinction coefficient: 0.00010 (2)
 62 parameters

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
W1	0.5	0.25	0.334530 (12)	0.01088 (5)
Ho1	0.75	0.325113 (17)	0.5	0.00662 (5)
K1	0.96872 (15)	0.07992 (10)	0.34389 (5)	0.0196 (2)
P1	0.75	0.07042 (10)	0.5	0.0065 (2)
O1	0.7088 (4)	0.2796 (3)	0.38536 (17)	0.0146 (7)
O2	0.4420 (6)	0.3643 (4)	0.2845 (2)	0.0269 (8)
O3	0.7308 (4)	-0.0047 (2)	0.43834 (16)	0.0102 (6)
O4	0.9229 (4)	0.1514 (2)	0.49215 (17)	0.0105 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
W1	0.01432 (9)	0.01167 (9)	0.00666 (9)	-0.00095 (8)	0	0
Ho1	0.00652 (9)	0.00523 (9)	0.00811 (10)	0	-0.00005 (9)	0
K1	0.0204 (4)	0.0248 (5)	0.0137 (4)	-0.0002 (4)	0.0021 (3)	0.0039 (4)
P1	0.0064 (5)	0.0034 (5)	0.0098 (6)	0	0.0000 (5)	0
O1	0.0154 (14)	0.0171 (14)	0.0113 (14)	-0.0035 (11)	-0.0012 (11)	-0.0031 (11)

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O2	0.0308 (17)	0.0296 (19)	0.0203 (17)	-0.0008 (17)	0.0013 (15)	0.0126 (16)
O3	0.0126 (13)	0.0079 (11)	0.0101 (13)	-0.0018 (10)	-0.0002 (11)	-0.0010 (9)
O4	0.0052 (10)	0.0066 (11)	0.0198 (16)	-0.0017 (9)	0.0011 (10)	-0.0016 (11)

Geometric parameters (\AA , $^\circ$)

W1—O2 ⁱ	1.749 (4)	Ho1—K1 ^{vii}	3.8119 (11)
W1—O2	1.749 (4)	Ho1—K1 ^{vi}	3.8119 (12)
W1—O1	1.788 (3)	K1—O3	2.683 (3)
W1—O1 ⁱ	1.788 (3)	K1—O2 ^v	2.689 (4)
W1—K1	3.8352 (12)	K1—O3 ^x	2.747 (3)
W1—K1 ⁱ	3.8352 (12)	K1—O1 ^{vi}	2.916 (3)
W1—K1 ⁱⁱ	4.0181 (13)	K1—O2 ^{xi}	2.934 (5)
W1—K1 ⁱⁱⁱ	4.0181 (13)	K1—O4	3.063 (3)
W1—K1 ^{iv}	4.0821 (12)	K1—O1	3.122 (4)
W1—K1 ^v	4.0821 (12)	K1—O2 ⁱ	3.133 (4)
Ho1—O4 ^{vi}	2.274 (3)	K1—P1	3.4251 (11)
Ho1—O4 ^{vii}	2.274 (3)	K1—Ho1 ^{vi}	3.8119 (11)
Ho1—O1	2.342 (3)	K1—K1 ⁱⁱⁱ	3.9511 (13)
Ho1—O1 ^{viii}	2.342 (3)	P1—O3	1.525 (3)
Ho1—O3 ^{ix}	2.401 (3)	P1—O3 ^{viii}	1.525 (3)
Ho1—O3 ⁱⁱ	2.401 (3)	P1—O4	1.552 (3)
Ho1—O4 ^{viii}	2.428 (3)	P1—O4 ^{viii}	1.552 (3)
Ho1—O4	2.428 (3)	P1—Ho1 ^{xii}	2.9802 (13)
Ho1—P1 ^{ix}	2.9802 (13)	P1—K1 ^{viii}	3.4251 (11)
Ho1—P1	3.0941 (13)		
O2 ⁱ —W1—O2	111.4 (3)	O3 ^x —K1—O4	61.07 (8)
O2 ⁱ —W1—O1	106.94 (17)	O1 ^{vi} —K1—O4	69.23 (9)
O2—W1—O1	109.83 (19)	O2 ^{xi} —K1—O4	130.90 (10)
O2 ⁱ —W1—O1 ⁱ	109.83 (19)	O3—K1—O1	76.52 (9)
O2—W1—O1 ⁱ	106.94 (17)	O2 ^v —K1—O1	100.44 (12)
O1—W1—O1 ⁱ	111.9 (2)	O3 ^x —K1—O1	117.21 (9)
O4 ^{vi} —Ho1—O4 ^{vii}	165.59 (15)	O1 ^{vi} —K1—O1	84.72 (10)
O4 ^{vi} —Ho1—O1	94.81 (11)	O2 ^{xi} —K1—O1	156.62 (10)
O4 ^{vii} —Ho1—O1	88.59 (11)	O4—K1—O1	58.09 (8)
O4 ^{vi} —Ho1—O1 ^{viii}	88.59 (11)	O3—K1—O2 ⁱ	77.94 (10)
O4 ^{vii} —Ho1—O1 ^{viii}	94.81 (11)	O2 ^v —K1—O2 ⁱ	78.50 (9)
O1—Ho1—O1 ^{viii}	152.68 (18)	O3 ^x —K1—O2 ⁱ	156.48 (11)
O4 ^{vi} —Ho1—O3 ^{ix}	88.91 (10)	O1 ^{vi} —K1—O2 ⁱ	131.64 (12)
O4 ^{vii} —Ho1—O3 ^{ix}	78.65 (10)	O2 ^{xi} —K1—O2 ⁱ	103.49 (13)
O1—Ho1—O3 ^{ix}	133.18 (11)	O4—K1—O2 ⁱ	101.64 (9)
O1 ^{viii} —Ho1—O3 ^{ix}	73.88 (12)	O1—K1—O2 ⁱ	54.04 (10)

O4 ^{vi} —Ho1—O3 ⁱⁱ	78.65 (10)	O3—P1—O3 ^{viii}	106.4 (2)
O4 ^{vii} —Ho1—O3 ⁱⁱ	88.91 (10)	O3—P1—O4	111.52 (16)
O1—Ho1—O3 ⁱⁱ	73.88 (12)	O3 ^{viii} —P1—O4	113.10 (16)
O1 ^{viii} —Ho1—O3 ⁱⁱ	133.18 (12)	O3—P1—O4 ^{viii}	113.10 (16)
O3 ^{ix} —Ho1—O3 ⁱⁱ	61.17 (15)	O3 ^{viii} —P1—O4 ^{viii}	111.52 (16)
O4 ^{vi} —Ho1—O4 ^{viii}	126.77 (7)	O4—P1—O4 ^{viii}	101.3 (2)
O4 ^{vii} —Ho1—O4 ^{viii}	67.63 (12)	W1—O1—Ho1	133.20 (16)
O1—Ho1—O4 ^{viii}	78.27 (12)	W1—O1—K1 ^{vi}	124.93 (16)
O1 ^{viii} —Ho1—O4 ^{viii}	78.03 (12)	Ho1—O1—K1 ^{vi}	92.27 (11)
O3 ^{ix} —Ho1—O4 ^{viii}	133.56 (10)	W1—O1—K1	99.08 (14)
O3 ⁱⁱ —Ho1—O4 ^{viii}	143.86 (10)	Ho1—O1—K1	111.49 (12)
O4 ^{vi} —Ho1—O4	67.63 (12)	K1 ^{vi} —O1—K1	86.88 (9)
O4 ^{vii} —Ho1—O4	126.77 (8)	W1—O2—K1 ^v	132.6 (2)
O1—Ho1—O4	78.03 (12)	W1—O2—K1 ⁱⁱ	115.89 (19)
O1 ^{viii} —Ho1—O4	78.27 (12)	K1 ^v —O2—K1 ⁱⁱ	95.86 (13)
O3 ^{ix} —Ho1—O4	143.86 (10)	W1—O2—K1 ⁱ	99.64 (16)
O3 ⁱⁱ —Ho1—O4	133.56 (10)	K1 ^v —O2—K1 ⁱ	120.18 (15)
O4 ^{viii} —Ho1—O4	59.26 (13)	K1 ⁱⁱ —O2—K1 ⁱ	81.21 (11)
O3—K1—O2 ^v	152.62 (12)	P1—O3—Ho1 ^{xii}	96.20 (15)
O3—K1—O3 ^x	78.69 (8)	P1—O3—K1	105.64 (14)
O2 ^v —K1—O3 ^x	124.78 (11)	Ho1 ^{xii} —O3—K1	130.32 (12)
O3—K1—O1 ^{vi}	119.65 (10)	P1—O3—K1 ⁱⁱⁱ	142.66 (16)
O2 ^v —K1—O1 ^{vi}	86.67 (12)	Ho1 ^{xii} —O3—K1 ⁱⁱⁱ	95.30 (9)
O3 ^x —K1—O1 ^{vi}	60.35 (9)	K1—O3—K1 ⁱⁱⁱ	93.37 (11)
O3—K1—O2 ^{xi}	93.55 (11)	P1—O4—Ho1 ^{vi}	146.28 (18)
O2 ^v —K1—O2 ^{xi}	78.59 (14)	P1—O4—Ho1	99.72 (13)
O3 ^x —K1—O2 ^{xi}	80.53 (10)	Ho1 ^{vi} —O4—Ho1	111.83 (11)
O1 ^{vi} —K1—O2 ^{xi}	118.34 (11)	P1—O4—K1	89.66 (13)
O3—K1—O4	52.05 (8)	Ho1 ^{vi} —O4—K1	89.92 (10)
O2 ^v —K1—O4	148.06 (12)	Ho1—O4—K1	110.96 (11)

Symmetry codes: (i) $-x+1, -y+1/2, z$; (ii) $-x+3/2, y+1/2, z$; (iii) $x-1/2, -y, z$; (iv) $x-1/2, y, -z+1/2$; (v) $-x+3/2, -y+1/2, -z+1/2$; (vi) $-x+2, -y+1/2, z$; (vii) $x-1/2, -y+1/2, -z+1$; (viii) $-x+3/2, y, -z+1$; (ix) $x, y+1/2, -z+1$; (x) $x+1/2, -y, z$; (xi) $-x+3/2, y-1/2, z$; (xii) $x, y-1/2, -z+1$.

Fig. 1

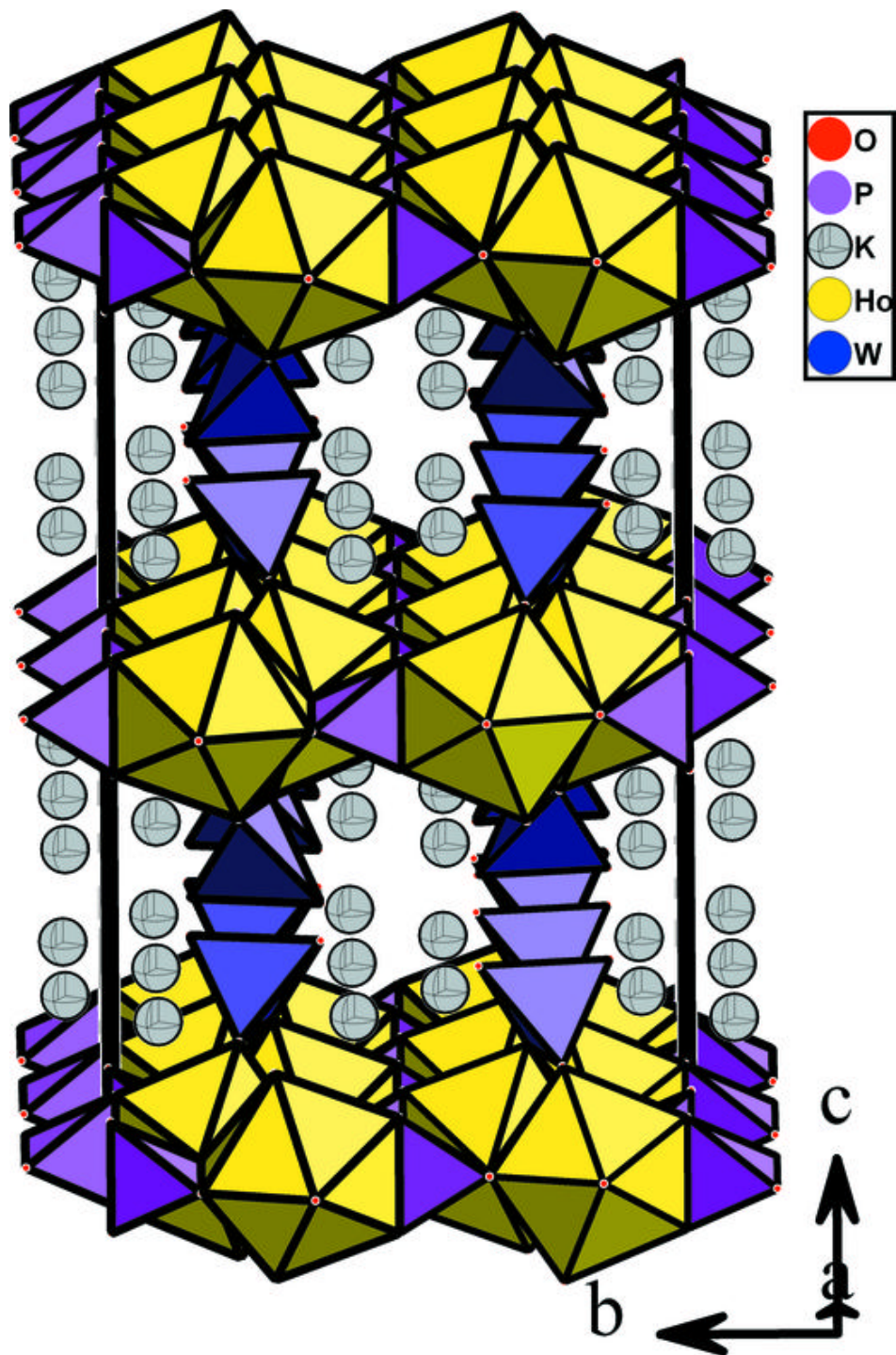


Fig. 2

