

A monoclinic polymorph of $\text{KY}(\text{PO}_3)_4$

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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{P}-\text{O}) = 0.006$ Å; R factor = 0.048; wR factor = 0.138; data-to-parameter ratio = 12.2.

The title compound, potassium yttrium polyphosphate, $\text{KY}(\text{PO}_3)_4$, was synthesized using the flux method. The atomic arrangement consists of an infinite long-chain polyphosphate organization. Chains, with a period of four PO_4 tetrahedra, run along the a -axis direction. Two other polymorphs of this phosphate are known, in space groups $P21/n$ and $C2/c$.

Related literature

For related structures, see: Durif (1995); Hamady *et al.* (1995); Hong *et al.* (1975); Malinowski (1990); Malinowski *et al.* (1988); Palkina *et al.* (1977). For earlier work on $\text{KY}(\text{PO}_3)_4$, see: Jouini *et al.* (2003). For related literature, see: Sun *et al.* (2004).

Experimental

Crystal data

$\text{KY}(\text{PO}_3)_4$	$V = 469.7$ (2) Å ³
$M_r = 443.89$	$Z = 2$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 7.2244$ (3) Å	$\mu = 7.40$ mm ⁻¹
$b = 8.2825$ (3) Å	$T = 298$ (2) K
$c = 7.854$ (4) Å	$0.16 \times 0.14 \times 0.13$ mm
$\beta = 91.735$ (3)°	

Data collection

Enraf–Nonius CAD-4 diffractometer	2011 independent reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 1996)	1904 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.321$, $T_{\max} = 0.376$	$R_{\text{int}} = 0.081$
3651 measured reflections	2 standard reflections
	every 150 reflections
	intensity decay: 2%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$	$\Delta\rho_{\text{max}} = 1.19$ e Å ⁻³
$wR(F^2) = 0.138$	$\Delta\rho_{\text{min}} = -2.67$ e Å ⁻³
$S = 1.13$	Absolute structure: Flack (1983),
2011 reflections	with 867 Friedel pairs
165 parameters	Flack parameter: 0.002 (9)
1 restraint	

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2073).

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Comment

Yttrium condensed phosphates have been considered as a crystal hosts for optical materials when doped with lanthanides, due to their high-temperature chemical stability, high yield intrinsic fluorescence and minimal trapping of excitation, rendering them attractive materials for investigations of the energy transfer phenomena and fluorescence quenching (Malinowski, 1990; Malinowski *et al.*, 1988). The literature dealing with these compounds was rather confusing for some time, between cyclic or chain condensed phosphates, but it is currently well established that the $M^I\text{Y}(\text{PO}_3)_4$ compounds are polyphosphates with infinite chain and $M^I\text{YP}_4\text{O}_{12}$ are cyclotetraphosphates (with M^I = monovalent cation) (Durif, 1995). In our laboratory we have synthesized the potassium and yttrium polyphosphates to establish the solid–liquid equilibrium diagram of the KPO_3 – $\text{Y}(\text{PO}_3)_3$ system (Jouini *et al.*, 2003). Three allotropic phases with the space groups $P2_1$, $P2_1/n$ and $C2/c$ were isolated and characterized. The three monoclinic allotropes are: i) $\text{KY}(\text{PO}_3)_4$ polyphosphate with the $P2_1$ space group, isostructural with $\text{KNd}(\text{PO}_3)_4$ (Hong, 1975). ii) $\text{KY}(\text{PO}_3)_4$ polyphosphate belongs to $P2_1/n$ space group, and is isostructural with $\text{TlNd}(\text{PO}_3)_4$ (Palkina *et al.*, 1977). In these two forms the phosphate anion has a chain structure. iii) The third allotropic form is $\text{KYP}_4\text{O}_{12}$ which crystallizes in the $C2/c$ space group, only this structure was investigated (Hamady, 1995). This paper is devoted to the crystal structure of the first polymorph $\text{KY}(\text{PO}_3)_4$ ($P2_1$). The atomic arrangement of this structure is characterized by a three-dimensional framework built of $(\text{PO}_3)_n$ chains that are formed by corner-sharing of PO_4 tetrahedra (Figs 1,2). The chains run along the a axis, with four PO_4 tetrahedra in a repeating unit. $\text{KY}(\text{PO}_3)_4$ is isostructural with $\text{KNd}(\text{PO}_3)_4$, but not with $\text{CsLa}(\text{PO}_3)_4$ (Sun *et al.*, 2004) although they belong to the same space group, $P2_1$. In the latter, the infinite screw $(\text{PO}_3)_n$ chains are repeated after every eighth PO_4 group along the b axis. The chains (two per unit cell) are joined to each other by YO_8 polyhedra (Fig 3.), no O atom is shared with the adjacent YO_8 polyhedra. The K atoms are in an eightfold coordination.

Experimental

Single crystal of $\text{KY}(\text{PO}_3)_4$ was prepared by flux method. Homogeneous solution of potassium carbonate K_2CO_3 (6 g) and yttrium oxide Y_2O_3 (0.5 g) containing a large excess of orthophosphoric acid H_3PO_4 (16 ml, 85% concentration) was heated in a vitreous carbon crucible at 473 K for 1 day. Then the temperature of the furnace was slowly raised to the predetermined temperature in the range of 573–623 K for 7 days. Crystals were separated from the excess phosphoric acid by washing the product in boiling water.

Refinement

The highest peak and the deepest hole are located 0.09 Å and 0.85 Å from Y.

Figures

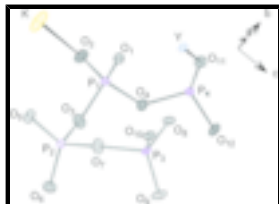


Fig. 1. : Projection of $\text{KY}(\text{PO}_3)_4$ with anisotropic displacement parameters drawn at the 50% probability level.

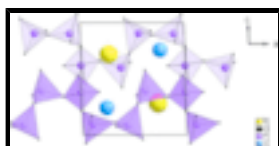


Fig. 2. : The structural arrangement of $\text{KY}(\text{PO}_3)_4$ along the b axis.

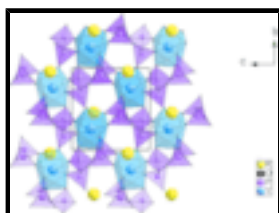


Fig. 3. : Projection of $\text{KY}(\text{PO}_3)_4$ along the a axis, showing isolated YO_8 polyhedra joined to $(\text{PO}_3)_n$ chains.

Potassium yttrium polyphosphate

Crystal data

$\text{KY}(\text{PO}_3)_4$

$M_r = 443.89$

Monoclinic, $P2_1$

Hall symbol: P 2yb

$a = 7.2244(3) \text{ \AA}$

$b = 8.2825(3) \text{ \AA}$

$c = 7.854(4) \text{ \AA}$

$\beta = 91.735(3)^\circ$

$V = 469.7(2) \text{ \AA}^3$

$Z = 2$

$F_{000} = 428$

$D_x = 3.138 \text{ Mg m}^{-3}$

Melting point: 760 K

Mo $K\alpha$ radiation

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

Cell parameters from 25 reflections

$\theta = 2.6\text{--}27.5^\circ$

$\mu = 7.40 \text{ mm}^{-1}$

$T = 298(2) \text{ K}$

Prism, colourless

$0.16 \times 0.14 \times 0.13 \text{ mm}$

Data collection

Enraf-Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298(2) \text{ K}$

$\omega/2\theta$ scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.321$, $T_{\max} = 0.376$

3651 measured reflections

$R_{\text{int}} = 0.081$

$\theta_{\max} = 27.5^\circ$

$\theta_{\min} = 2.6^\circ$

$h = -7 \rightarrow 9$

$k = -8 \rightarrow 10$

$l = -8 \rightarrow 10$

2 standard reflections

every 150 reflections

2011 independent reflections
1904 reflections with $I > 2\sigma(I)$

intensity decay: 2%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0908P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.138$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.13$	$\Delta\rho_{\max} = 1.19 \text{ e } \text{\AA}^{-3}$
2011 reflections	$\Delta\rho_{\min} = -2.67 \text{ e } \text{\AA}^{-3}$
165 parameters	Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001x Fc^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
1 restraint	Extinction coefficient: 0.065 (7)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), with 867 Friedel pairs Flack parameter: 0.002 (9)

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R-factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Y	0.23704 (8)	0.75897 (9)	0.24245 (8)	0.0086 (3)
K	0.2703 (3)	0.4566 (3)	-0.2812 (3)	0.0303 (6)
P1	0.4367 (3)	0.3830 (2)	0.0947 (3)	0.0091 (4)
P2	0.0994 (3)	0.1755 (2)	0.0978 (2)	0.0086 (4)
P3	-0.0018 (3)	0.4085 (2)	0.3809 (2)	0.0088 (4)
P4	0.6161 (3)	0.5114 (2)	0.3992 (2)	0.0084 (4)
O1	0.3212 (8)	0.5292 (7)	0.0721 (7)	0.0140 (12)
O2	0.5736 (8)	0.3558 (8)	-0.0387 (8)	0.0184 (13)
O3	0.3126 (7)	0.2261 (7)	0.1093 (8)	0.0169 (13)
O4	0.5360 (8)	0.3706 (7)	0.2789 (7)	0.0139 (12)
O5	0.0239 (8)	0.2062 (7)	-0.0776 (7)	0.0150 (12)
O6	0.0880 (8)	0.0105 (7)	0.1732 (7)	0.0163 (12)
O7	-0.0076 (8)	0.2991 (7)	0.2159 (8)	0.0189 (13)
O8	0.1660 (7)	0.5100 (7)	0.3846 (7)	0.0124 (11)

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O9	-0.0337 (8)	0.3109 (7)	0.5348 (8)	0.0167 (12)
O10	-0.1755 (8)	0.5225 (7)	0.3407 (7)	0.0121 (11)
O11	0.5258 (8)	0.6648 (7)	0.3514 (7)	0.0138 (11)
O12	0.6118 (7)	0.4535 (7)	0.5773 (7)	0.0121 (11)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Y	0.0092 (4)	0.0103 (4)	0.0067 (4)	-0.0004 (3)	0.0048 (2)	-0.0001 (2)
K	0.0180 (10)	0.0601 (16)	0.0129 (8)	0.0108 (9)	0.0031 (7)	-0.0019 (10)
P1	0.0100 (9)	0.0098 (10)	0.0080 (9)	-0.0003 (7)	0.0044 (7)	-0.0004 (6)
P2	0.0084 (9)	0.0095 (9)	0.0082 (9)	-0.0008 (6)	0.0034 (7)	-0.0004 (7)
P3	0.0090 (9)	0.0107 (10)	0.0070 (9)	-0.0009 (7)	0.0055 (7)	0.0003 (7)
P4	0.0086 (9)	0.0088 (9)	0.0081 (8)	0.0003 (6)	0.0032 (7)	0.0001 (6)
O1	0.018 (3)	0.012 (3)	0.012 (3)	0.001 (2)	0.003 (2)	-0.001 (2)
O2	0.021 (3)	0.021 (3)	0.014 (3)	0.007 (2)	0.011 (2)	-0.001 (2)
O3	0.010 (3)	0.018 (3)	0.023 (3)	-0.003 (2)	0.000 (2)	-0.004 (2)
O4	0.016 (3)	0.015 (3)	0.011 (3)	0.001 (2)	-0.002 (2)	0.000 (2)
O5	0.014 (3)	0.020 (3)	0.011 (3)	0.004 (2)	0.002 (2)	-0.003 (2)
O6	0.019 (3)	0.011 (3)	0.019 (3)	0.003 (2)	-0.002 (2)	0.004 (2)
O7	0.018 (3)	0.020 (3)	0.019 (3)	0.003 (2)	0.008 (2)	-0.010 (2)
O8	0.008 (3)	0.016 (3)	0.013 (3)	-0.004 (2)	0.004 (2)	0.004 (2)
O9	0.017 (3)	0.019 (3)	0.015 (3)	0.003 (2)	0.010 (2)	0.007 (2)
O10	0.011 (3)	0.015 (3)	0.011 (3)	-0.002 (2)	0.005 (2)	0.003 (2)
O11	0.012 (3)	0.015 (3)	0.014 (3)	0.003 (2)	0.000 (2)	0.002 (2)
O12	0.010 (2)	0.019 (3)	0.008 (2)	0.005 (2)	0.002 (2)	0.000 (2)

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

Y—O2 ⁱ	2.282 (6)	P1—O1	1.479 (6)
Y—O5 ⁱⁱ	2.296 (6)	P1—O2	1.480 (6)
Y—O9 ⁱⁱⁱ	2.358 (6)	P1—O3	1.585 (6)
Y—O11	2.363 (5)	P1—O4	1.599 (5)
Y—O12 ^{iv}	2.387 (5)	P2—O5	1.488 (6)
Y—O6 ^v	2.400 (6)	P2—O6	1.492 (6)
Y—O8	2.408 (6)	P2—O3	1.597 (6)
Y—O1	2.415 (6)	P2—O7	1.597 (6)
Y—K ⁱ	3.921 (2)	P3—O8	1.474 (6)
K—O12 ^{vi}	2.736 (6)	P3—O9	1.478 (6)
K—O8 ^{vi}	2.744 (6)	P3—O7	1.581 (6)
K—O6 ⁱⁱ	2.785 (6)	P3—O10	1.594 (6)
K—O1	2.852 (6)	P4—O11	1.472 (6)
K—O9 ^{vi}	2.859 (7)	P4—O12	1.480 (6)
K—O11 ^{vii}	2.892 (7)	P4—O10 ^{viii}	1.590 (6)
K—O2	2.979 (6)	P4—O4	1.598 (6)
K—O5	3.194 (6)		

O2 ⁱ —Y—O5 ⁱⁱ	99.8 (2)	O9 ^{vi} —K—O11 ^{vii}	86.49 (17)
O2 ⁱ —Y—O9 ⁱⁱⁱ	148.9 (2)	O12 ^{vi} —K—O2	66.57 (16)
O5 ⁱⁱ —Y—O9 ⁱⁱⁱ	86.2 (2)	O8 ^{vi} —K—O2	146.32 (18)
O2 ⁱ —Y—O11	80.1 (2)	O6 ⁱⁱ —K—O2	121.50 (18)
O5 ⁱⁱ —Y—O11	147.3 (2)	O1—K—O2	50.68 (17)
O9 ⁱⁱⁱ —Y—O11	110.8 (2)	O9 ^{vi} —K—O2	138.0 (2)
O2 ⁱ —Y—O12 ^{iv}	84.6 (2)	O11 ^{vii} —K—O2	61.22 (17)
O5 ⁱⁱ —Y—O12 ^{iv}	144.7 (2)	O12 ^{vi} —K—O5	136.07 (19)
O9 ⁱⁱⁱ —Y—O12 ^{iv}	73.79 (19)	O8 ^{vi} —K—O5	116.25 (17)
O11—Y—O12 ^{iv}	67.98 (19)	O6 ⁱⁱ —K—O5	54.12 (17)
O2 ⁱ —Y—O6 ^v	79.1 (2)	O1—K—O5	72.96 (18)
O5 ⁱⁱ —Y—O6 ^v	71.5 (2)	O9 ^{vi} —K—O5	63.10 (17)
O9 ⁱⁱⁱ —Y—O6 ^v	74.0 (2)	O11 ^{vii} —K—O5	81.22 (17)
O11—Y—O6 ^v	138.9 (2)	O2—K—O5	84.71 (17)
O12 ^{iv} —Y—O6 ^v	75.09 (19)	O1—P1—O2	115.3 (4)
O2 ⁱ —Y—O8	140.1 (2)	O1—P1—O3	111.2 (3)
O5 ⁱⁱ —Y—O8	85.16 (19)	O2—P1—O3	108.5 (4)
O9 ⁱⁱⁱ —Y—O8	70.5 (2)	O1—P1—O4	113.4 (3)
O11—Y—O8	75.39 (19)	O2—P1—O4	109.9 (3)
O12 ^{iv} —Y—O8	113.77 (19)	O3—P1—O4	97.0 (3)
O6 ^v —Y—O8	138.4 (2)	O5—P2—O6	120.0 (3)
O2 ⁱ —Y—O1	73.9 (2)	O5—P2—O3	109.5 (3)
O5 ⁱⁱ —Y—O1	75.7 (2)	O6—P2—O3	106.4 (3)
O9 ⁱⁱⁱ —Y—O1	136.7 (2)	O5—P2—O7	104.9 (3)
O11—Y—O1	72.9 (2)	O6—P2—O7	108.9 (4)
O12 ^{iv} —Y—O1	137.92 (19)	O3—P2—O7	106.4 (3)
O6 ^v —Y—O1	132.6 (2)	O8—P3—O9	116.4 (4)
O8—Y—O1	69.1 (2)	O8—P3—O7	110.1 (3)
O12 ^{vi} —K—O8 ^{vi}	80.69 (17)	O9—P3—O7	110.9 (4)
O12 ^{vi} —K—O6 ⁱⁱ	169.5 (2)	O8—P3—O10	107.9 (3)
O8 ^{vi} —K—O6 ⁱⁱ	91.99 (17)	O9—P3—O10	110.2 (3)
O12 ^{vi} —K—O1	107.81 (17)	O7—P3—O10	100.1 (3)
O8 ^{vi} —K—O1	156.9 (2)	O11—P4—O12	120.0 (3)
O6 ⁱⁱ —K—O1	76.31 (17)	O11—P4—O10 ^{viii}	107.0 (3)
O12 ^{vi} —K—O9 ^{vi}	118.63 (18)	O12—P4—O10 ^{viii}	109.8 (3)
O8 ^{vi} —K—O9 ^{vi}	53.15 (16)	O11—P4—O4	109.3 (3)
O6 ⁱⁱ —K—O9 ^{vi}	60.95 (18)	O12—P4—O4	107.7 (3)
O1—K—O9 ^{vi}	130.90 (19)	O10 ^{viii} —P4—O4	101.5 (3)
O12 ^{vi} —K—O11 ^{vii}	56.23 (17)	P1—O3—P2	139.3 (4)
O8 ^{vi} —K—O11 ^{vii}	94.54 (19)	P4—O4—P1	129.2 (4)
O6 ⁱⁱ —K—O11 ^{vii}	132.5 (2)	P3—O7—P2	147.4 (4)

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O1—K—O11^{vii}

108.06 (18)

P4^{ix}—O10—P3

130.9 (4)

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

Fig. 1

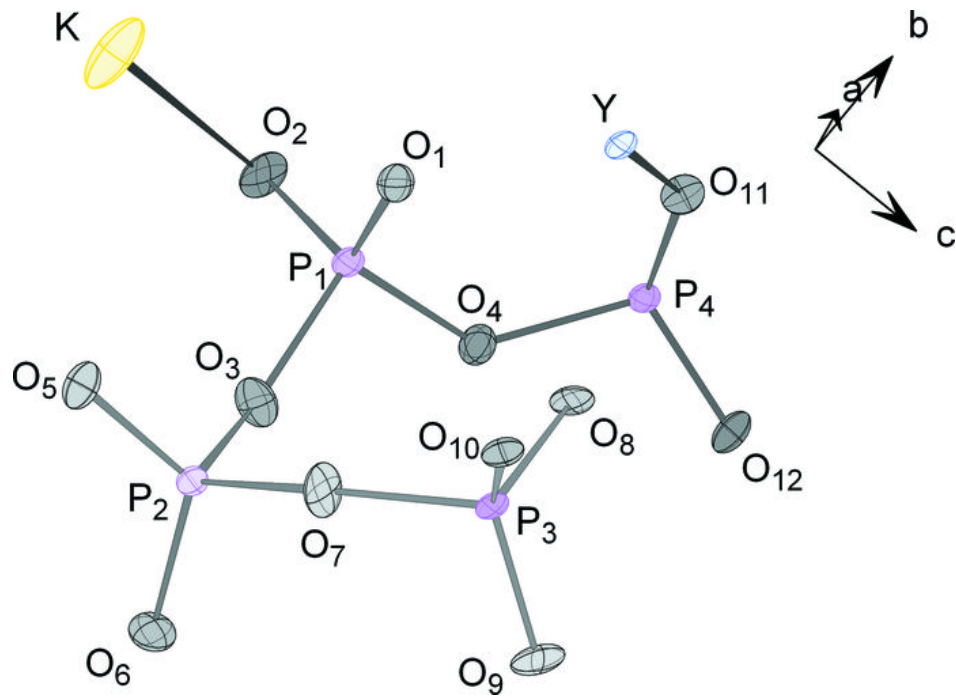


Fig. 2

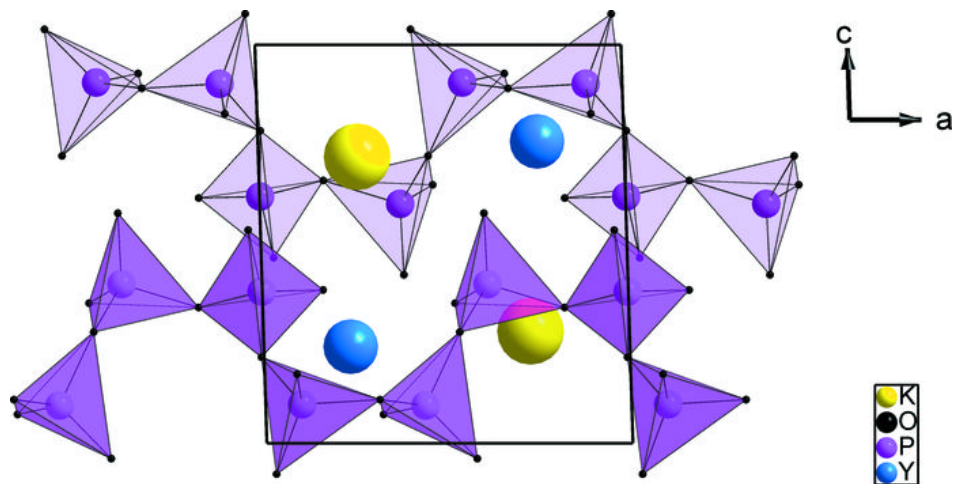


Fig. 3

