

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

K_{0.53}Mn_{2.37}Fe_{1.24}(PO₄)₃

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Received 3 November 2010; accepted 6 December 2010

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{Mn}-\text{O}) = 0.003$ Å; disorder in main residue; R factor = 0.037; wR factor = 0.089; data-to-parameter ratio = 12.8.

During an attempt to crystallize potassium manganese diiron phosphate $\text{KMnFe}_2(\text{PO}_4)_3$ by the flux method, a new phase, potassium dimanganese iron triphosphate, $\text{K}_{0.53}\text{Mn}_{2.37}\text{Fe}_{1.24}(\text{PO}_4)_3$, was isolated. This phase, whose composition was confirmed by ICP analysis, is isotopic with the alluaudite-like phosphates, thus it exhibits the $(A2)(A'2)(A1)(A'1)(A''1)-(M1)(M2)_2(\text{PO}_4)_3$ general formula. The site occupancies led to the following cation distribution: 0.53 K on $A'2$ (site symmetry 2), 0.31 Mn on $A''1$, 1.0 Mn on $M1$ (site symmetry 2) and (0.62 Fe + 0.38 Mn) on $M2$. The structure is built up from infinite chains of edge-sharing $M1\text{O}_6$ and $M2\text{O}_6$ octahedra. These chains run along $[10\bar{1}]$ and are connected by two different PO_4 tetrahedra, one of which exhibits 2 symmetry. The resulting three-dimensional framework delimits large tunnels parallel to $[001]$, which are partially occupied by the K^+ and Mn^{2+} cations.

Related literature

For the alluaudite structure, see: Fisher (1955); Moore (1971); Chouaibi *et al.* (2001); Corbin *et al.* (1986); Lee & Ye (1997); Hidouri *et al.* (2003, 2004, 2008) Antenucci *et al.* (1993, 1995); For P—O distances, see: Baur (1974). For bond-valence sums, see: Brown & Altermatt (1985). For ionic radii, see: Shannon (1976).

Experimental

Crystal data

$\text{K}_{0.53}\text{Mn}_{2.37}\text{Fe}_{1.24}(\text{PO}_4)_3$	$a = 12.272$ (2) Å
$M_r = 505.28$	$b = 12.606$ (2) Å
Monoclinic, $C2/c$	$c = 6.416$ (4) Å

$\beta = 114.87$ (2)°
 $V = 900.5$ (6) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 6.07$ mm⁻¹
 $T = 293$ K
 $0.43 \times 0.09 \times 0.02$ mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer	1308 independent reflections
Absorption correction: refined from ΔF (Parkin <i>et al.</i> , 1995)	1047 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.42$, $T_{\max} = 0.81$	$R_{\text{int}} = 0.042$
1754 measured reflections	2 standard reflections every 120 min
	intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	102 parameters
$wR(F^2) = 0.089$	2 restraints
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.78$ e Å ⁻³
1308 reflections	$\Delta\rho_{\text{min}} = -0.68$ e Å ⁻³

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2150).

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Acta Cryst. (2011). E67, i1 [doi:10.1107/S1600536810051238]

K_{0.53}Mn_{2.37}Fe_{1.24}(PO₄)₃

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Comment

The term alluaudite is referred to both natural and synthetic phosphates of compositions (Na⁺)(Na⁺, Ca²⁺)(M²⁺)(Fe²⁺, Fe³⁺)₂(PO₄)₃ where M²⁺ is a divalent cation. The first detailed structural description was reported in 1971 by Moore (Moore, 1971) who proposed the structural formula (X2)(X1)(M1)(M2)₂(PO₄)₃. X1 and X2 are cationic sites available to large monovalent and divalent cations such as Na⁺ and Ca²⁺ while M1 and M2 are octahedral sites containing a distribution of divalent and trivalent cations of moderate size such as Mn²⁺, Fe²⁺ or Fe³⁺. More recently, detailed structural analysis of several alluaudites demonstrated that the X2 site has two distinct positions labeled A2 (0, 0, 0) and A'2 (0, ~0, 1/4) in a tunnel at (0, 0, z) and X1 has three distinct positions, labeled A1 (1/2, 0, 0), A'1 (0, ~1/2, 1/4) and A''1 (x, y, z) in a tunnel at (1/2, 0, z). The general formula of Moore was then reformulated as [(A2)(A'2)][(A1)(A'1)(A''1)](M1)(M2)₂(PO₄)₃. The crystal structure consists of M₂O₁₀ bioctahedral units of edge-sharing M₂O₆ octahedra, sharing opposite edges with M₁O₆ octahedra that form zigzag chains of a sequence -M(2)-M(2)-M(1)-, running along the [1 0 - 1] direction. Adjacent chains are linked by the phosphate tetrahedra leading to what have been described as "pleated sheets" perpendicular to the [0 1 0] direction (Fig. 1(b)). These sheets are connected by the phosphate groups giving rise to a three-dimensional framework with two sets of tunnels parallel to [001] (Fig. 1(b)).

The title phase K_{0.53}Mn_{2.37}Fe_{1.24}(PO₄)₃ was isolated during an attempt to synthesize KMnFe₂(PO₄)₃ and its structure has shown to be of the alluaudite type. The site occupancy factors indicated to the following cation distribution: 0.53 K on A'2, 0.31 Mn on A''1, 1.0 Mn on M1 and (0.62 Fe + 0.38 Mn) on M2. The partial occupancy of the large A sites has already been observed in several alluaudites being attributed to the great flexibility of these sites which allows them to be filled totally, partially or left vacant without significant influence on the alluaudite framework. Assuming a maximum gap in the cation-oxygen distances, the environment of the A'2 site (figure 2) consists of eight oxygen atoms forming what has been called by Moore as a gable desphenoid (Moore, 1971). That of the A''1 site (figure 2) consists of five O atoms forming a distorted trigonal bipyramid. The fivefold coordination of this site which is, to the best of our knowledge, observed for the first time in an alluaudite-like compound can be attributed to the small size of the Mn²⁺ cation. Both the M1 and M2 sites are octahedrally coordinated (figure 2). From the M1—O distances and *cis* O—M1—O angles, one can deduce that the M₁O₆ octahedron is strongly distorted. However, the mean M1—O mean distance of 2.238 Å is close to that 2.23 Å predicted by Shannon for octahedral Mn²⁺ cations (Shannon, 1976). The M2—O distances and *cis* O—M2—O angles show the M₂O₆ octahedron to be less distorted than M₁O₆. The <M(2)—O> mean distance (2.068 Å) is between 2.03 Å and 2.23 Å, calculated by Shannon (Shannon, 1976) for the Fe³⁺ and Mn²⁺ cations, respectively. This result confirms the presence of both atoms on the M(2) site. The PO₄ tetrahedra have classical P—O distances with an overall value of 1.537 Å close to that 1.537 Å, assigned by Baur for the monophosphate groups (Baur, 1974). The Bond Valence Sums (BVS) were calculated for all cationic sites by the Brown and Altermatt method (Brown *et al.*, 1985). The analysis of the sums for the M2 site, around Fe³⁺ and Mn²⁺ led to valence sums of 2.87 and 2.64, respectively which corresponds to occupation numbers of 0.71 and

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0.29, very close to the x-ray values of 0.62 and 0.38. The sum around Mn3 is 1.34 and around K is 0.42. These are poor because of the partial occupancy but unfortunately these values cannot be used to estimate the occupancy. The sums around P1 and P2 of 4.92 and 4.98, respectively around the O sites (from 1.91 to 2.12) are consistent with the predicted ones of 5 for P and 2 for O. In summary, the valence calculation results gave a good confirmation of the structure, including the assigned oxidation states which cannot be determined by x-ray analysis.

Experimental

Single crystals of the title phase were extracted from a mixture of nominal composition $\text{KMnFe}_2(\text{PO}_4)_3$. The latter was prepared by the flux method starting from a mixture of 2.042 g of KNO_3 , 2.589 g of $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 8.245 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 4.002 g of $(\text{NH}_4)_2\text{HPO}_4$ and 0.719 g of MoO_3 . These reactants were dissolved in nitric acid and the solution obtained was dried for 24 h at 353 K. The obtained dry residue was ground in an agate mortar to ensure its best homogeneity, then heated in a platinum crucible to 673 K for 24 h in order to remove the decomposition products: NH_3 and H_2O . The sample was then reground, melted at 1173 K for 1 h and subsequently cooled at a $10^\circ \cdot \text{h}^{-1}$ rate to 673 K. The final product was washed with warm water in order to dissolve the flux. From the mixture, dark brown and hexagonally shaped crystals were extracted. Their analysis using ICP confirmed the presence of only K, Mn, Fe and P in atomic ratio of 0.53:2.37:1.24:3, in accordance with the $\text{K}_{0.53}\text{Mn}_{2.37}\text{Fe}_{1.24}(\text{PO}_4)_3$ composition.

Figures

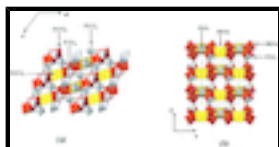


Fig. 1. Polyhedral representations of the $\text{K}_{0.53}\text{Mn}_{2.37}\text{Fe}_{1.24}(\text{PO}_4)_3$ structure as projected along $[010]$ (a) and along $[001]$ (b). M1O_6 , M2O_6 are represented by yellow and red octahedra, respectively and PO_4 by crossed tetrahedra.

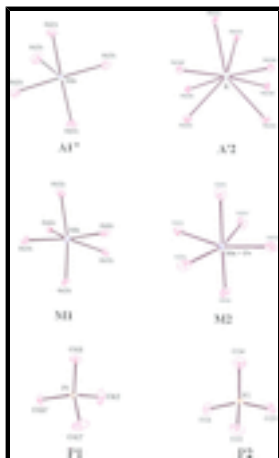


Fig. 2. The environments of the A^1 , A^2 , $M1$, $M2$, $P1$ and $P2$ sites showing the anisotropic atomic displacements. The thermal ellipsoids are drawn at 50 % probability level.

Potassium dimanganese iron triphosphate

Crystal data

$\text{K}_{0.53}\text{Mn}_{2.37}\text{Fe}_{1.24}(\text{PO}_4)_3$

$M_r = 505.28$

Monoclinic, $C2/c$

$F(000) = 957$

$D_x = 3.727 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Hall symbol: -C 2yc
 $a = 12.272 (2) \text{ \AA}$
 $b = 12.606 (2) \text{ \AA}$
 $c = 6.416 (4) \text{ \AA}$
 $\beta = 114.87 (2)^\circ$
 $V = 900.5 (6) \text{ \AA}^3$
 $Z = 4$

Cell parameters from 25 reflections
 $\theta = 9.8\text{--}14.4^\circ$
 $\mu = 6.07 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Hexagonal, brown
 $0.43 \times 0.09 \times 0.02 \text{ mm}$

Data collection

Enraf–Nonius TurboCAD-4
 diffractometer

1047 reflections with $I > 2\sigma(I)$

Radiation source: fine-focus sealed tube
 graphite

$R_{\text{int}} = 0.042$

non-profiled $\omega/2\theta$ scans

$\theta_{\text{max}} = 30.0^\circ$, $\theta_{\text{min}} = 2.4^\circ$

Absorption correction: part of the refinement model
 (ΔF)
 (Parkin *et al.*, 1995)

$h = -17 \rightarrow 15$

$T_{\text{min}} = 0.42$, $T_{\text{max}} = 0.81$

$k = 0 \rightarrow 17$

1754 measured reflections

$l = 0 \rightarrow 9$

1308 independent reflections

2 standard reflections every 120 min

intensity decay: 1%

Refinement

Refinement on F^2

Primary atom site location: structure-invariant direct methods

Least-squares matrix: full

Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.037$

$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$wR(F^2) = 0.089$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$S = 1.07$

$\Delta\rho_{\text{max}} = 0.78 \text{ e \AA}^{-3}$

1308 reflections

$\Delta\rho_{\text{min}} = -0.67 \text{ e \AA}^{-3}$

102 parameters

Extinction correction: *SHELXL97* (Sheldrick, 2008)

2 restraints

Extinction coefficient: 0.0009 (4)

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.

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 $F^2 > \sigma(F^2)$ 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.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
K	0.0000	-0.0116 (2)	0.2500	0.0229 (7)	0.531 (5)
Mn1	0.0000	0.26376 (7)	0.2500	0.0156 (2)	
Fe2	0.22489 (4)	0.15521 (4)	0.13977 (8)	0.01004 (16)	0.6217 (6)
Mn2	0.22489 (4)	0.15521 (4)	0.13977 (8)	0.01004 (16)	0.3783 (7)
Mn3	-0.02360 (17)	0.49774 (17)	0.0393 (4)	0.0209 (5)	0.3064 (12)
P1	0.0000	0.28642 (11)	-0.2500	0.0096 (3)	
O11	0.0479 (2)	0.2160 (2)	-0.0331 (4)	0.0138 (5)	
O12	-0.0942 (3)	0.3615 (2)	-0.2314 (6)	0.0251 (7)	
P2	0.24436 (8)	0.10810 (7)	0.63905 (15)	0.0093 (2)	
O21	0.2272 (2)	0.1782 (2)	0.8220 (4)	0.0156 (6)	
O22	0.1735 (3)	0.1629 (2)	0.4048 (4)	0.0169 (6)	
O23	0.3783 (2)	0.1019 (2)	0.6976 (6)	0.0255 (7)	
O24	0.1930 (2)	-0.0019 (2)	0.6349 (5)	0.0178 (6)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K	0.0093 (10)	0.0218 (13)	0.0260 (13)	0.000	-0.0040 (9)	0.000
Mn1	0.0115 (4)	0.0202 (4)	0.0154 (4)	0.000	0.0058 (3)	0.000
Fe2	0.0065 (2)	0.0138 (3)	0.0065 (3)	0.00016 (18)	-0.00043 (19)	0.0008 (2)
Mn2	0.0065 (2)	0.0138 (3)	0.0065 (3)	0.00016 (18)	-0.00043 (19)	0.0008 (2)
Mn3	0.0156 (12)	0.0164 (9)	0.0165 (11)	-0.0002 (9)	-0.0070 (7)	0.0014 (9)
P1	0.0060 (5)	0.0140 (6)	0.0038 (5)	0.000	-0.0028 (4)	0.000
O11	0.0087 (11)	0.0193 (13)	0.0066 (11)	-0.0027 (10)	-0.0033 (9)	0.0028 (10)
O12	0.0149 (13)	0.0245 (15)	0.0301 (17)	0.0025 (12)	0.0037 (13)	-0.0119 (14)
P2	0.0065 (4)	0.0123 (4)	0.0050 (4)	0.0004 (3)	-0.0016 (3)	0.0012 (3)
O21	0.0128 (12)	0.0235 (14)	0.0078 (11)	-0.0030 (11)	0.0017 (10)	-0.0038 (11)
O22	0.0244 (14)	0.0141 (14)	0.0048 (11)	0.0003 (11)	-0.0010 (10)	-0.0007 (10)
O23	0.0114 (13)	0.0189 (15)	0.047 (2)	0.0003 (11)	0.0132 (14)	-0.0018 (15)
O24	0.0127 (12)	0.0184 (14)	0.0171 (13)	-0.0013 (11)	0.0012 (11)	0.0030 (11)

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

K—O24	2.608 (3)	Mn1—O22 ⁱ	2.315 (3)
K—O24 ⁱ	2.608 (3)	Mn1—O22	2.315 (3)
K—O24 ⁱⁱ	2.767 (3)	Fe2—O24 ⁱⁱ	1.970 (3)
K—O24 ⁱⁱⁱ	2.767 (3)	Fe2—O12 ^x	2.027 (3)
K—O11 ^{iv}	2.869 (4)	Fe2—O22	2.049 (3)
K—O11 ^v	2.869 (4)	Fe2—O21 ^{xi}	2.071 (3)
K—O22	2.929 (3)	Fe2—O11	2.123 (3)
K—O22 ⁱ	2.929 (3)	Fe2—O21 ^{vi}	2.167 (3)
Mn3—O23 ^{vi}	2.253 (4)	P1—O12 ^{xii}	1.537 (3)
Mn3—O23 ^{vii}	2.256 (4)	P1—O12	1.537 (3)

Mn3—O12 ^{viii}	2.294 (4)	P1—O11 ^{xii}	1.544 (3)
Mn3—O12	2.335 (4)	P1—O11	1.544 (3)
Mn3—O23 ^{ix}	2.400 (4)	P2—O24	1.519 (3)
Mn1—O23 ^{vi}	2.189 (3)	P2—O23	1.526 (3)
Mn1—O23 ^{vii}	2.189 (3)	P2—O22	1.547 (3)
Mn1—O11	2.215 (3)	P2—O21	1.553 (3)
Mn1—O11 ⁱ	2.215 (3)		
O24—K—O24 ⁱ	174.63 (16)	O23 ^{vi} —Mn1—O11	86.39 (11)
O24—K—O24 ⁱⁱ	73.24 (8)	O23 ^{vii} —Mn1—O11	118.95 (12)
O24 ⁱ —K—O24 ⁱⁱ	106.42 (8)	O23 ^{vi} —Mn1—O11 ⁱ	118.95 (12)
O24—K—O24 ⁱⁱⁱ	106.42 (8)	O23 ^{vii} —Mn1—O11 ⁱ	86.39 (11)
O24 ⁱ —K—O24 ⁱⁱⁱ	73.24 (8)	O11—Mn1—O11 ⁱ	148.43 (15)
O24 ⁱⁱ —K—O24 ⁱⁱⁱ	172.95 (16)	O23 ^{vi} —Mn1—O22 ⁱ	159.42 (10)
O24—K—O11 ^{iv}	114.87 (10)	O23 ^{vii} —Mn1—O22 ⁱ	85.06 (10)
O24 ⁱ —K—O11 ^{iv}	70.34 (8)	O11—Mn1—O22 ⁱ	90.70 (10)
O24 ⁱⁱ —K—O11 ^{iv}	87.10 (9)	O11 ⁱ —Mn1—O22 ⁱ	71.87 (10)
O24 ⁱⁱⁱ —K—O11 ^{iv}	99.26 (10)	O23 ^{vi} —Mn1—O22	85.06 (10)
O24—K—O11 ^v	70.34 (8)	O23 ^{vii} —Mn1—O22	159.42 (10)
O24 ⁱ —K—O11 ^v	114.87 (10)	O11—Mn1—O22	71.87 (10)
O24 ⁱⁱ —K—O11 ^v	99.26 (10)	O11 ⁱ —Mn1—O22	90.70 (10)
O24 ⁱⁱⁱ —K—O11 ^v	87.10 (9)	O22 ⁱ —Mn1—O22	113.36 (14)
O11 ^{iv} —K—O11 ^v	52.22 (11)	O24 ⁱⁱ —Fe2—O12 ^x	94.65 (12)
O24—K—O22	53.32 (8)	O24 ⁱⁱ —Fe2—O22	86.05 (12)
O24 ⁱ —K—O22	121.80 (11)	O12 ^x —Fe2—O22	109.44 (13)
O24 ⁱⁱ —K—O22	57.49 (9)	O24 ⁱⁱ —Fe2—O21 ^{xi}	101.92 (12)
O24 ⁱⁱⁱ —K—O22	116.43 (11)	O12 ^x —Fe2—O21 ^{xi}	87.13 (12)
O11 ^{iv} —K—O22	144.11 (8)	O22—Fe2—O21 ^{xi}	161.16 (11)
O11 ^v —K—O22	122.58 (8)	O24 ⁱⁱ —Fe2—O11	101.11 (11)
O24—K—O22 ⁱ	121.80 (11)	O12 ^x —Fe2—O11	162.62 (11)
O24 ⁱ —K—O22 ⁱ	53.32 (8)	O22—Fe2—O11	79.18 (11)
O24 ⁱⁱ —K—O22 ⁱ	116.43 (11)	O21 ^{xi} —Fe2—O11	82.52 (11)
O24 ⁱⁱⁱ —K—O22 ⁱ	57.49 (9)	O24 ⁱⁱ —Fe2—O21 ^{vi}	174.59 (11)
O11 ^{iv} —K—O22 ⁱ	122.58 (8)	O12 ^x —Fe2—O21 ^{vi}	81.71 (11)
O11 ^v —K—O22 ⁱ	144.11 (8)	O22—Fe2—O21 ^{vi}	91.37 (11)
O22—K—O22 ⁱ	82.66 (13)	O21 ^{xi} —Fe2—O21 ^{vi}	81.97 (11)
O23 ^{vi} —Mn3—O23 ^{vii}	75.91 (14)	O11—Fe2—O21 ^{vi}	83.04 (10)
O23 ^{vi} —Mn3—O12 ^{viii}	84.68 (13)	O12 ^{xii} —P1—O12	104.0 (3)
O23 ^{vii} —Mn3—O12 ^{viii}	121.62 (16)	O12 ^{xii} —P1—O11 ^{xii}	107.33 (17)
Mn1 ^{viii} —Mn3—O12	76.0 (3)	O12—P1—O11 ^{xii}	114.23 (15)
O23 ^{vi} —Mn3—O12	94.38 (14)	O12 ^{xii} —P1—O11	114.23 (15)
O23 ^{vii} —Mn3—O12	79.85 (14)	O12—P1—O11	107.33 (17)

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O12 ^{viii} —Mn3—O12	157.20 (11)	O11 ^{xii} —P1—O11	109.7 (2)
Mn1 ^{viii} —Mn3—O23 ^{ix}	69.7 (3)	O24—P2—O23	110.71 (16)
O23 ^{vi} —Mn3—O23 ^{ix}	157.58 (11)	O24—P2—O22	109.32 (15)
O23 ^{vii} —Mn3—O23 ^{ix}	123.93 (15)	O23—P2—O22	111.67 (18)
O12 ^{viii} —Mn3—O23 ^{ix}	91.62 (14)	O24—P2—O21	110.22 (17)
O12—Mn3—O23 ^{ix}	80.58 (13)	O23—P2—O21	108.50 (16)
O23 ^{vi} —Mn1—O23 ^{vii}	78.61 (15)	O22—P2—O21	106.32 (16)

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

Fig. 1

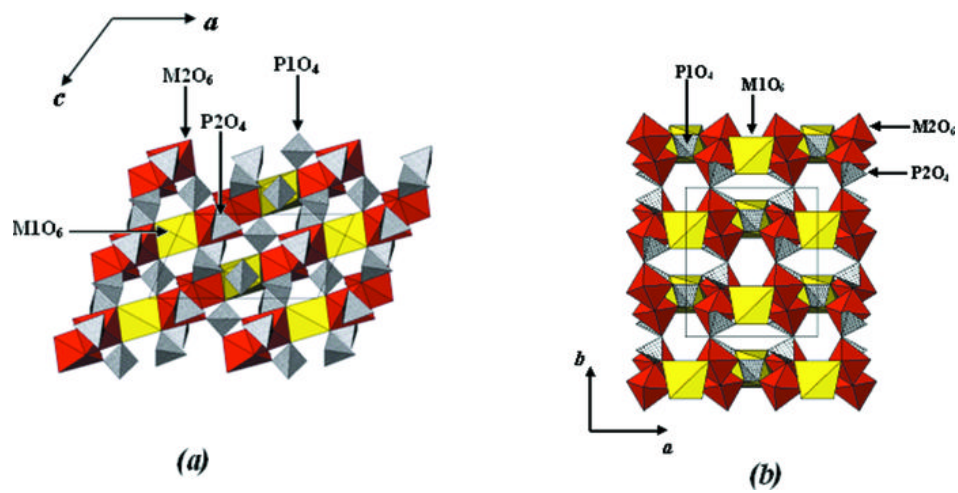


Fig. 2

