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Rietveld refinement of whitlockite-related $K_{0.8}Ca_{9.8}Fe_{0.2}(PO_4)_7$

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Key indicators: powder X-ray study; T = 293 K; mean σ(P–O) = 0.024 Å; disorder in main residue; R factor = 8.711; wR factor = 11.243; data-to-parameter ratio = 5.4.

The title compound, $K_{0.8}Ca_{9.8}Fe_{0.2}(PO_4)_7$ (potassium decacalcium iron heptaphosphate), belongs to the whitlockite family. The structure is built up from several types of metal–oxygen polyhedra: two $[CaO_8]$, one $[CaO_7]$ and one $[(Ca/Fe)O_6]$ polyhedron with a mixed Ca/Fe occupancy in a 0.8:0.2 ratio, as well as three tetrahedral $[PO_4]$ units. Of the 18 sites in the asymmetric unit, the site with the mixed Ca/Fe occupation, the K site, one P and one O site are on special positions 6a with 3 symmetry, whereas all other sites are on general positions 18b. The linkage of metal–oxygen polyhedra and $[PO_4]$ tetrahedra *via* edges and corners results in formation of a three-dimensional framework with composition $[Ca_{9.8}Fe_{0.2}(PO_4)_7]^{0.8-}$. The remaining K atoms (site-occupation factor = 0.8) are located in large closed cavities and are nine-coordinated by oxygen.

Related literature

For the structure of the mineral whitlockite with idealized composition $Ca_3(PO_4)_2$ (β-polymorph), see: Calvo & Gopal (1975); Yashima *et al.* (2003). For $KCa_{10}(PO_4)_7$, see: Sandström & Boström (2006). For powder diffraction investigations and Rietveld refinements of other phosphate-based whitlockites, see: Morozov *et al.* (2000) for $M^ICa_{10}(PO_4)_7$ (M^I = Li, Na, K); Lazoryak *et al.* (1996) for $Ca_9Fe(PO_4)_7$; Morozov *et al.* (2002) for $Ca_9In(PO_4)_7$; Strunenkova *et al.* (1997) for $Na_{1.5}Ca_9Fe_{0.5}(PO_4)_7$. For the profile function used in the Rietveld refinement, see: Thompson *et al.* (1987).

Experimental

Crystal data

$K_{0.8}Ca_{9.8}Fe_{0.2}(PO_4)_7$
M_r = 1100.02
Trigonal, $R3c$
a = 10.44282 (1) Å
c = 37.29443 (3) Å
V = 3522.17 (1) Å^3
Z = 6
Cu $K\alpha$ radiation, λ = 1.540598 Å
T = 293 K
Flat sheet, 25 × 25 mm

Data collection

Shimadzu LabX XRD-6000 diffractometer
Specimen mounting: glass container
Data collection mode: reflection
Scan method: step
$2\theta_{min}$ = 8.92°, $2\theta_{max}$ = 99.92°, increment in 2θ = 0.02°

Refinement

R_p = 8.711
R_{wp} = 11.243
R_{exp} = 4.919
R_{Bragg} = 3.849
$R(F)$ = 2.48
4551 data points with 839 reflections
131 parameters
4 restraints

Table 1
Selected bond lengths (Å).

Ca1—O11^{i}	2.519 (10)	Ca3—O31^{vii}	2.47 (4)
Ca1—O21^{ii}	2.702 (13)	Ca3—O33^{vii}	2.78 (3)
Ca1—O22	2.51 (3)	Ca3—O34	2.60 (3)
Ca1—O23^{ii}	2.40 (2)	Ca4—O24	2.30 (3)
Ca1—O32	2.579 (17)	Ca4—O31	2.23 (4)
Ca1—O32^{iii}	2.57 (2)	Fe4—O24	2.30 (3)
Ca1—O33^{iii}	2.59 (3)	Fe4—O31	2.23 (4)
Ca1—O34	2.48 (3)	K1—O12	2.90 (3)
Ca2—O12^{ii}	2.474 (16)	K1—O21	2.508 (19)
Ca2—O23^{iv}	2.63 (3)	K1—O22	3.25 (3)
Ca2—O24^{iv}	2.444 (19)	P1—O11	1.51 (4)
Ca2—O24^{v}	2.48 (3)	P1—O12	1.62 (2)
Ca2—O32^{v}	2.41 (2)	P2—O21	1.49 (2)
Ca2—O33^{iii}	2.21 (3)	P2—O22	1.56 (2)
Ca2—O34	2.36 (3)	P2—O23	1.53 (2)
Ca3—O12	2.295 (15)	P2—O24	1.486 (17)
Ca3—O21	2.48 (2)	P3—O31	1.62 (3)
Ca3—O22^{vi}	2.49 (3)	P3—O32	1.53 (3)
Ca3—O23^{iv}	2.30 (3)	P3—O33	1.57 (3)
Ca3—O31	2.38 (3)	P3—O34	1.63 (2)

Symmetry codes: (i) $-x+y+\frac{2}{3}, y+\frac{1}{3}, z-\frac{1}{6}$; (ii) $-x+y, -x, z$; (iii) $-y+1, x-y, z$; (iv) $x+\frac{1}{3}, x-y+\frac{2}{3}, z+\frac{1}{6}$; (v) $-x+y+\frac{1}{3}, y-\frac{1}{3}, z+\frac{1}{6}$; (vi) $-y+\frac{1}{3}, -x+\frac{2}{3}, z+\frac{1}{6}$; (vii) $-x+y, -x+1, z$.

Data collection: *PCXRD* (Shimadzu, 2006); cell refinement: *DICVOL 2004* (Boultif & Louër, 2004); data reduction: *FULLPROF* (Rodriguez-Carvajal, 2006); program(s) used to solve structure: *FULLPROF*; program(s) used to refine structure: *FULLPROF*; molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *PLATON* (Spek, 2009) and *enCIFer* (Allen *et al.*, 2004).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2324).

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supplementary materials

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Rietveld refinement of whitlockite-related $K_{0.8}Ca_{9.8}Fe_{0.2}(PO_4)_7$

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Comment

In the compound $K_{0.8}Ca_{9.8}Fe_{0.2}(PO_4)_7$, (I), atoms Ca4/Fe4, K1, P1 and O11 are in special positions 6*a* that lie on a 3-fold rotation axis, whereas all other atoms are located in general positions 18*b* (Fig. 1).

Compound (I) might be represented as a result of an aliovalent substitution of calcium atoms in β-$Ca_3(PO_4)_2$ (Calvo *et al.*, 1975; Yashima *et al.*, 2003) by a pair of K and Fe atoms.

[CaO_x] polyhedra (two types of [CaO_8], one of [CaO_7] and one [(Ca/Fe)O_6] with mixed Fe/Ca occupancy) and three different [PO_4] tetrahedra are linked via edges and corners to built a three-dimensional framework with composition $[Ca_{9.8}Fe_{0.2}(PO_4)_7]^{0.8-}$ (Fig. 2). The K^+ cations are located in large closed cavities inside the framework (K1 occupancy is equal to 0.8).

For (I), Ca—O distances of [CaO_8]- and [CaO_7]-polyhedra (2.295 (15)-2.78 (3) Å) are close to these in previously reported isotypic compounds *s*-$Ca_9Fe(PO_4)_7$ (2.29 (3)-2.73 (3) Å), *o*-$Ca_9Fe(PO_4)_7$ (2.29 (3)-2.70 (4) Å) (Lazoryak *et al.*, 1996) and $KCa_{10}(PO_4)_7$ (2.329 (3)- 2.76 (2) Å) (Sandström & Boström, 2006). The distances Ca/Fe—O (2.23 (4)-2.29 (3) Å) within the [(Ca/Fe)O_6] polyhedron are close to these of the [CaO_6] polyhedron in $KCa_{10}(PO_4)_7$ (2.239 (4)-2.267 (4) Å), while they significantly differ from *d*(Fe—O) = 1.95 (3)-2.17 (3) Å in $Ca_9Fe(PO_4)_7$.

Potassium atoms are nine-coordinated (three triples of K—O distances in the range of 2.508 (19)-3.24 (3) Å) (Fig. 3), while in $KCa_{10}(PO_4)_7$ the K—O contacts vary in the range of 2.641 (3)-3.25 (4) Å .

In conclusion, compound (I) can be considered as a solid solution within the $KCa_{10}(PO_4)_7$ / $Ca_9Fe(PO_4)_7$ double system.

Experimental

The title compound was prepared by solid state reaction from a mixture of K_2CO_3, $CaCO_3$, Fe_2O_3 and $NH_4H_2PO_4$ in the molar ratio K/Ca/Fe/P = 0.8:9.8:0.2:7.0. The reagents were finely ground in an agate mortar and then placed in a porcelain crucible. The thermal treatment was carried out in three steps. The first included preheating to 873 K to decompose the ammonium salt and carbonates. After that, the mixture was heated at 1273 K for 12 h, cooled to room temperature, reground, and held at 1373 K for 6 h. The resulting product was a pale pink powder.

Refinement

The powder pattern was indexed in rhombohedral cell (hexagonal setting) by *Dicvol 2004* (Boultif & Louër, 2004). The structure of $KCa_{10}(PO_4)_7$ (Sandström & Boström, 2006) was selected as a starting model for Rietveld refinement. Profile matching refinement was performed firstly. Then scaling factor and background were added to the refined parameters. The background was approximated using linear interpolation between a set of background points with refineable heights. A modified pseudo-Voigt function (Thompson *et al.*, 1987) was used for the profile refinement. As it was determined previously, only one position of calcium is suitable for heterovalent substitution by a three-valent 3*d*-metal. It is the octahedrally coordinated Ca4 site. Thus the iron site was placed into the Ca4 position. The occupancy of iron was fixed at 0.2 while the remaining calcium occupancy was set to 0.8. The potassium occupancy was set to 0.8 due to electroneutrality of the compound. The atomic coordinates and B_{iso} of Ca and Fe were constrained to be equal. ADPs of all P atoms were constrained to be equal as well as the ADPs of all O atoms. The value of B_{iso} for Ca4 was restrained in the range of 0.17-0.3. The value of B_{iso} for O11 was also restrained in the range of 0.2-0.3. Two distance restraints for P2—O21 and P2—O23 bonds were applied. Experimental, calculated and difference patterns after the final refinement cycle are shown in Fig. 4.

Figures

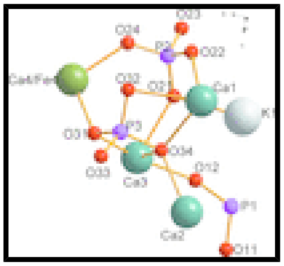

Fig. 1. A view of the unit cell content of compound (I).

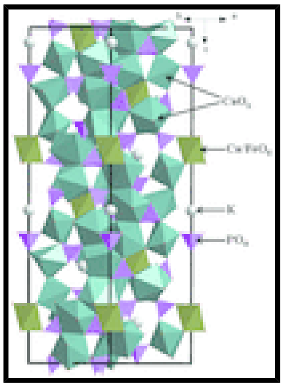

Fig. 2. Connectivity of the metal-oxygen polyhedra and PO_4 groups in (I).

Fig. 3. Coordination environment of the atoms in 6*a* position.

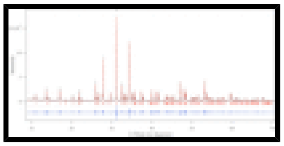

Fig. 4. Rietveld refinement of $K_{0.8}Ca_{9.8}Fe_{0.2}(PO_4)_7$. Experimental (dots), calculated (red curve) and difference (blue curve) data for 2θ range 9-72°.

potassium decacalcium iron heptaphosphate

Crystal data

$K_{0.8}Ca_{9.8}Fe_{0.2}(PO_4)_7$
$M_r = 1100.02$
Trigonal, *R*3*c*
Hall symbol: R 3 -2"c
$a = 10.44282$ (1) Å

$D_x = 3.112$ Mg m^{-3}
Cu *K*α radiation, λ = 1.540598 Å
$T = 293$ K
Particle morphology: isometric
light pink

c = 37.29443 (3) Å	flat_sheet, 25 × 25 mm
V = 3522.17 (1) Å^3	Specimen preparation: Prepared at 293 K and 101.3 kPa
Z = 6	

Data collection

Shimadzu LabX XRD-6000 diffractometer	Data collection mode: reflection
Radiation source: X-ray tube, X-ray	Scan method: step
graphite	$2\theta_{min}$ = 8.91°, $2\theta_{max}$ = 99.92°, $2\theta_{step}$ = 0.02°
Specimen mounting: glass container	

Refinement

R_p = 8.711	Profile function: Thompson–Cox–Hastings pseudo-Voigt * Axial divergence asymmetry
R_{wp} = 11.243	131 parameters
R_{exp} = 4.919	4 restraints
R_{Bragg} = 3.849	4 constraints
$R(F)$ = 2.48	Standard least squares refinement
χ^2 = 5.368	$(\Delta/\sigma)_{max}$ = 0.001
4551 data points	Background function: Linear Interpolation between a set background points with refinable heights
Excluded region(s): undef	Preferred orientation correction: Modified March's Function

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

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

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Ca1	0.3986 (5)	0.1868 (7)	0.0212 (4)	0.0022 (18)*	
Ca2	0.3922 (6)	0.1887 (10)	0.1265 (4)	0.0022 (16)*	
Ca3	0.1776 (11)	0.3817 (6)	0.0949 (5)	0.003 (2)*	
Ca4	0.33333	0.66667	0.0288 (5)	0.002 (2)*	0.80000
Fe4	0.33333	0.66667	0.0288 (5)	0.002 (2)*	0.20000
K1	0.00000	0.00000	0.0447 (5)	0.004 (4)*	0.80000
P1	0.00000	0.00000	0.1293 (5)	0.0031 (11)*	
P2	0.1351 (9)	0.3124 (6)	−0.0032 (4)	0.0031 (11)*	
P3	0.4897 (11)	0.4749 (11)	0.0609 (5)	0.0031 (11)*	
O11	0.00000	0.00000	0.1699 (8)	0.0025 (11)*	
O12	0.0071 (19)	0.1449 (14)	0.1115 (7)	0.0025 (11)*	
O21	0.0912 (15)	0.2697 (15)	0.0349 (4)	0.0025 (11)*	
O22	0.222 (2)	0.233 (2)	−0.0145 (6)	0.0025 (11)*	

O23	−0.0066 (16)	0.265 (2)	−0.0248 (5)	0.0025 (11)*
O24	0.229 (3)	0.4728 (17)	−0.0110 (6)	0.0025 (11)*
O31	0.408 (3)	0.567 (3)	0.0709 (7)	0.0025 (11)*
O32	0.5039 (17)	0.4689 (16)	0.0203 (5)	0.0025 (11)*
O33	0.6427 (19)	0.5475 (19)	0.0808 (6)	0.0025 (11)*
O34	0.3720 (19)	0.3100 (19)	0.0752 (7)	0.0025 (11)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
?	?	?	?	?	?	?

Geometric parameters (Å, °)

Ca1—O11^{i}	2.519 (10)	Ca4—O31^{viii}	2.229 (35)
Ca1—O21^{ii}	2.702 (13)	Fe4—O24^{viii}	2.299 (30)
Ca1—O22	2.509 (26)	Fe4—O24	2.299 (30)
Ca1—O23^{ii}	2.397 (20)	Fe4—O24^{vii}	2.299 (30)
Ca1—O32	2.579 (17)	Fe4—O31	2.229 (35)
Ca1—O32^{iii}	2.573 (23)	Fe4—O31^{vii}	2.229 (35)
Ca1—O33^{iii}	2.591 (27)	Fe4—O31^{viii}	2.229 (35)
Ca1—O34	2.479 (28)	K1—O12	2.896 (30)
Ca2—O12^{ii}	2.474 (16)	K1—O12^{ii}	2.896 (30)
Ca2—O23^{iv}	2.629 (26)	K1—O12^{ix}	2.896 (30)
Ca2—O24^{iv}	2.444 (19)	K1—O21	2.508 (19)
Ca2—O24^{v}	2.484 (33)	K1—O21^{ii}	2.508 (19)
Ca2—O32^{v}	2.410 (23)	K1—O21^{ix}	2.508 (19)
Ca2—O33^{iii}	2.207 (27)	K1—O22	3.245 (26)
Ca2—O34	2.362 (29)	K1—O22^{ii}	3.245 (26)
Ca3—O12	2.295 (15)	K1—O22^{ix}	3.245 (26)
Ca3—O21	2.477 (22)	P1—O11	1.51 (4)
Ca3—O22^{vi}	2.485 (29)	P1—O12	1.62 (2)
Ca3—O23^{iv}	2.301 (25)	P1—O12^{ix}	1.62 (2)
Ca3—O31	2.383 (25)	P1—O12^{ii}	1.62 (2)
Ca3—O31^{vii}	2.468 (36)	P2—O21	1.49 (2)
Ca3—O33^{vii}	2.781 (25)	P2—O22	1.56 (2)
Ca3—O34	2.597 (27)	P2—O23	1.53 (2)
Ca4—O24^{viii}	2.299 (30)	P2—O24	1.486 (17)
Ca4—O24	2.299 (30)	P3—O31	1.62 (3)
Ca4—O24^{vii}	2.299 (30)	P3—O32	1.53 (3)
Ca4—O31	2.229 (35)	P3—O33	1.57 (3)
Ca4—O31^{vii}	2.229 (35)	P3—O34	1.63 (2)
O24—Fe4—O24^{vii}	82.8 (11)	O22—P2—O23	114.2 (13)
O24—Fe4—O31^{vii}	101.7 (10)	O22—P2—O24	108.3 (15)

O24^{viii}—Fe4—O31	101.6 (10)	O23—P2—O24	104.3 (15)
O31—Fe4—O31^{viii}	75.9 (12)	O31—P3—O32	110.2 (15)
O24^{vii}—Fe4—O31	175.2 (13)	O31—P3—O33	108.4 (15)
O31—Fe4—O31^{vii}	75.9 (14)	O31—P3—O34	102.1 (15)
O24^{viii}—Fe4—O31^{viii}	99.6 (11)	O32—P3—O33	113.1 (14)
O24^{viii}—Fe4—O24^{vii}	82.8 (11)	O32—P3—O34	108.6 (13)
O24^{viii}—Fe4—O31^{vii}	175.2 (12)	O33—P3—O34	113.8 (14)
O24^{vii}—Fe4—O31^{viii}	101.7 (11)	O12^{ix}—P1—O12^{ii}	104.3 (12)
O31^{viii}—Fe4—O31^{vii}	75.9 (13)	O11—P1—O12^{ii}	114.2 (11)
O24^{vii}—Fe4—O31^{vii}	99.6 (13)	O11—P1—O12	114.2 (11)
O24—Fe4—O31	99.6 (9)	O11—P1—O12^{ix}	114.2 (11)
O24—Fe4—O24^{viii}	82.8 (11)	O12—P1—O12^{ix}	104.4 (12)
O24—Fe4—O31^{viii}	175.2 (12)	O12—P1—O12^{ii}	104.4 (13)
O21—P2—O22	105.8 (12)	Fe4—O24—P2	128.4 (15)
O21—P2—O23	107.5 (11)	Fe4—O31—P3	121.8 (16)
O21—P2—O24	117.0 (13)		

Symmetry codes: (i) $-x+y+2/3$, $y+1/3$, $z-1/6$; (ii) $-x+y$, $-x$, z; (iii) $-y+1$, $x-y$, z; (iv) $x+1/3$, $x-y+2/3$, $z+1/6$; (v) $-x+y+1/3$, $y-1/3$, $z+1/6$; (vi) $-y+1/3$, $-x+2/3$, $z+1/6$; (vii) $-x+y$, $-x+1$, z; (viii) $-y+1$, $x-y+1$, z; (ix) $-y$, $x-y$, z.

Fig. 1

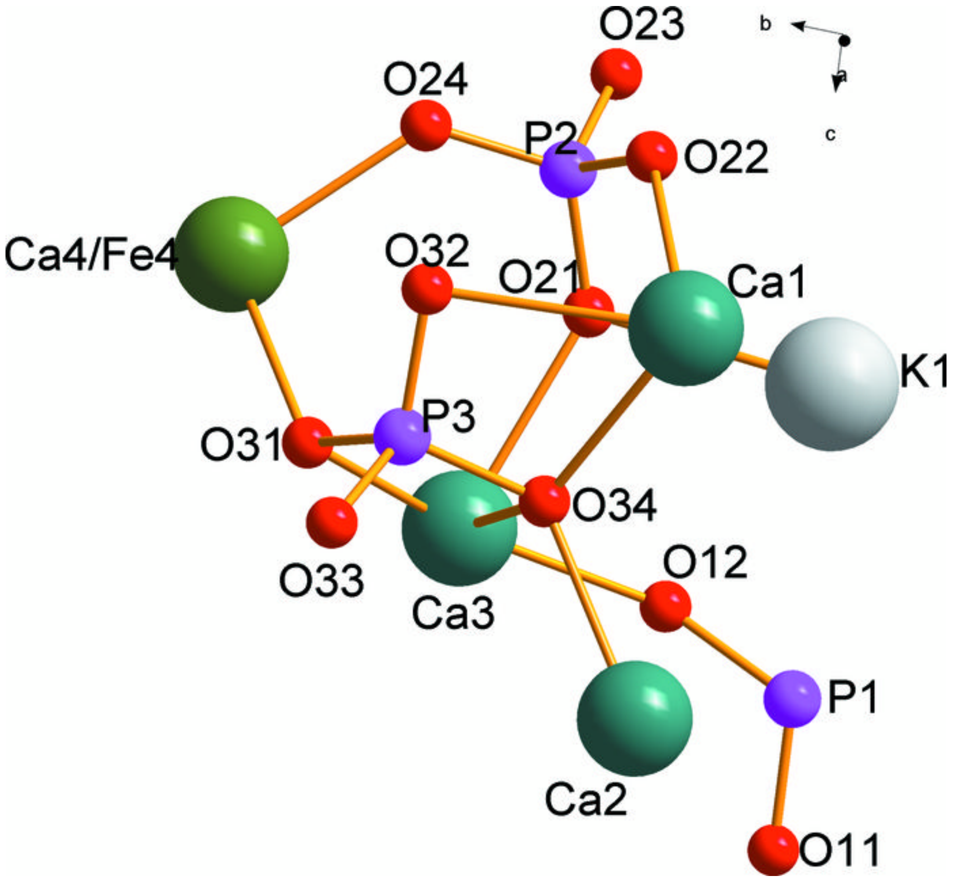
O23
b
a
c
O24
P2
O22
Ca4/Fe4
O32
O21
Ca1
K1
O31
P3
O34
O33
Ca3
O12
P1
Ca2
O11

Fig. 2

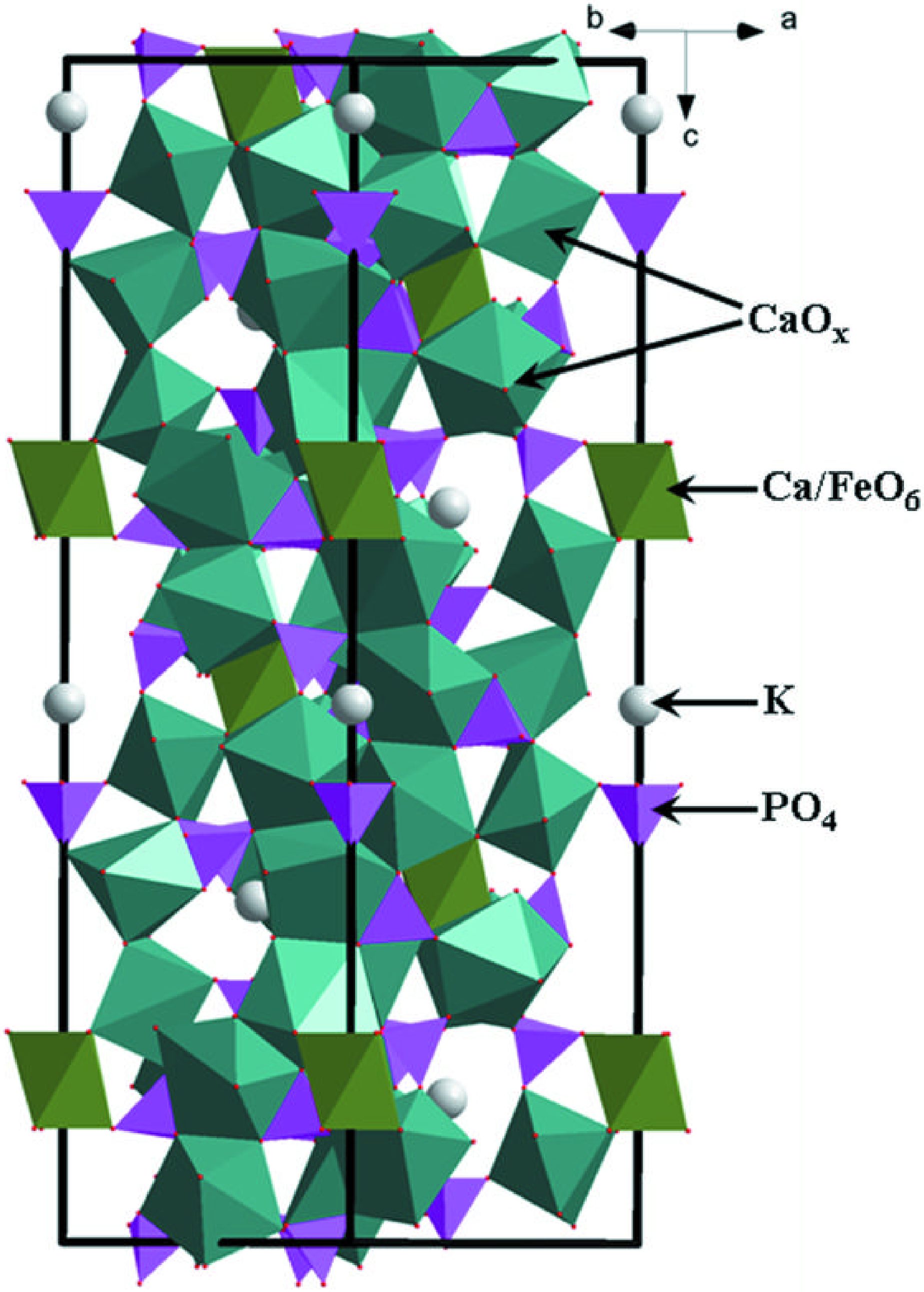

Fig. 3

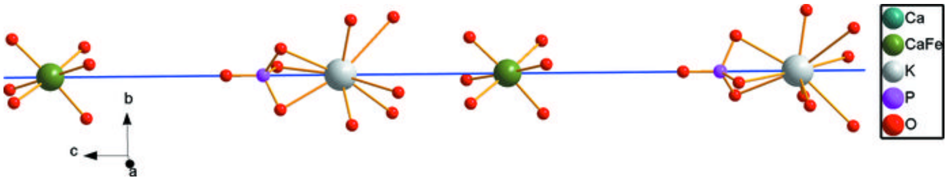

Fig. 4