son aimable contribution à l'enregistrement des données.

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Non-Stoichiometry in the $KMo_2P_3O_{12}$-Tunnel Structure: the Oxide $K_{0.75}MoNbP_3O_{12}$

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Abstract. $K_{0.75}MoNbP_3O_{12}$, $M_r = 503{\cdot}009$, orthorhombic, *Pbcm*, $a = 8{\cdot}8518$ (5), $b = 9{\cdot}1453$ (11), $c = 12{\cdot}5174$ (11) Å, $V = 1013{\cdot}3$ (3) Å^3, $Z = 4$, $D_x = 3{\cdot}300$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 3{\cdot}13$ mm^{-1}, $F(000) = 953$, $T = 294$ K, $R = 0{\cdot}029$, $wR = 0{\cdot}033$ for 1235 observed reflections. This compound is isostructural with $KMo_2P_3O_{12}$-type oxides. Its framework is built up from MoO_6 octahedra and PO_4 tetrahedra which delimit tunnels running along **b**. Different from $KMo_2P_3O_{12}$, the tunnels are partly occupied by the potassium ions which are distributed at random.

Introduction. Comparison of niobium and molybdenum phosphates shows that the mixed frameworks of these oxides, built up from NbO_6 or MoO_6 octahedra and PO_4 tetrahedra, are very different in spite of the existence of both elements in oxidation states IV and V. The difference observed for the Mo^V phosphates is not unexpected, owing to the particular electronic structure of this cation which leads to an abnormally short Mo—O distance as shown, for instance, by α-$KMo_2P_3O_{13}$ (Leclaire, Monier & Raveau, 1983), α- and β-$CsMoP_3O_{13}$ (Lii & Haushalter, 1987), β-$RbMo_2P_3O_{13}$ (Riou & Goreaud, 1989), γ-$CsMo_2P_3O_{13}$ (Chen, Lii & Wang, 1988), δ-$KMo_2P_3O_{13}$ (Leclaire, Borel, Grandin & Raveau, 1989*a*) and $AMo_5P_8O_{33}$ (A = Li, Na, Ag) (Lii, Johnston, Goshorn & Haushalter, 1987). But the niobium phosphates differ also from the molybdenum phosphates by the existence of mixed-valence compounds Nb^V–Nb^{IV} characterized by a delocalization of the electrons as shown for the oxides $KNb_3P_3O_{15}$ (Leclaire, Borel, Grandin & Raveau, 1989*b*), $K_7Nb_{14}P_9O_{60}$ (Leclaire, Benabbas, Borel, Grandin & Raveau, 1989) and $K_3Nb_6P_4O_{26}$ (Benabbas, Borel, Grandin, Leclaire & Raveau, 1990). The most surprising feature concerns the comparison of Nb^{IV} and Mo^{IV}. Although MoO_2 and NbO_2 belong to the same rutile-type structure, under the same experimental conditions we obtain different results for the same formulation. For molybdenum, $KMo_2P_3O_{12}$ (Leclaire & Raveau, 1988) with Mo^{IV} only is obtained whereas, for niobium, we always obtain phases with mixed-valence niobium phosphates: $Nb_2P_3O_{12}$ (Leclaire, Borel, Grandin & Raveau, 1989*c*) and $Na_{0.5}Nb_2P_3O_{12}$ (Leclaire, Borel, Grandin & Raveau, 1990). In order to understand this difference, an attempt to substitute niobium for molybdenum in the oxide $KMo_2P_3O_{12}$ was made. We report here the crystal structure of the oxide $K_{0.75}MoNbP_3O_{12}$.

Experimental. The synthesis was performed in two steps. First $H(NH_4)_2PO_4$, MoO_3, Nb_2O_5 and K_2CO_3 were mixed in an agate mortar in the molecular ratio to obtain the stoichiometry $KMo_{0.5}NbP_3O_{12}$ and heated in air to decompose the potassium carbonate and the ammonium phosphate. The resulting mixture was then added to the required amount of molybdenum and placed in an evacuated silica ampoule. This mixture was heated for 5 d at 1373 K and then

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Table 1. *Atomic parameters*

$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2abc\cos\gamma)\beta_{12} + (2ac\cos\beta)\beta_{13} + (2bc\cos\alpha)\beta_{23}]$.

	x	y	z	B_{eq}(Å^2)
Mo—Nb	0·24695 (7)	0·02586 (4)	0·10063 (3)	0·68 (1)
K	−0·17042 (67)	0·15917 (50)	0·25000	5·15 (14)
P(1)	−0·02884 (19)	0·25000	0·00000	0·69 (2)
P(2)	0·40255 (15)	0·36752 (16)	0·13221 (12)	0·74 (2)
O(1)	0·20537 (65)	0·01597 (71)	0·25000	1·21 (10)
O(2)	0·12745 (49)	−0·15602 (49)	0·07173 (39)	1·62 (8)
O(3)	0·30155 (48)	0·04000 (51)	−0·06273 (34)	1·45 (8)
O(4)	0·37812 (53)	0·20556 (44)	0·12177 (37)	1·55 (8)
O(5)	0·43106 (44)	−0·10142 (50)	0·12188 (37)	1·65 (9)
O(6)	0·06527 (43)	0·15356 (50)	0·07317 (36)	1·46 (8)
O(7)	0·35151 (62)	0·41444 (70)	0·25000 (0)	1·04 (10)

quenched to room temperature. Some suitable black crystals were extracted from the sintered product. The composition $K_{0\cdot75}MoNbP_3O_{12}$ was deduced from microprobe analysis and confirmed by the crystal structure.

Black crystal, 0·096 × 0·072 × 0·0036 mm; symmetry *mmm* with systematic absences 0*kl* for *k* odd and *h*0*l* for *l* odd. Space group *Pbcm*; Enraf–Nonius CAD-4 diffractometer. Unit cell: least squares on 25 reflections $\pm 2\theta$, $36 \le 2\theta \le 44°$. Intensity measurement by $\omega - \frac{2}{3}\theta$ scan of $(1 + 0\cdot35\tan\theta)°$ and $(1 + \tan\theta)$ mm counter slit determined by a study of same reflection in the $\omega\theta$ plane. Scan speed adjusted to obtain $\sigma(I)/I \le 0\cdot018$ or to approach it in a time limited to 60 s. Three standards for count (006, 004, 113) every 2000 s and orientation (006, 440, 200) every 600 reflections: no appreciable trends. Of 4180 measured, 1235 reflections ($h_{max} = 17$, $k_{max} = 18$, $l_{max} = 24$), $2 \le \theta \le 45°$, with $I/\sigma(I) \ge 3$ used to solve and refine the structure. No correction made for extinction or absorption. All subsequent calculations on an IBM 3090 by local adaptation of the classical programs; atomic scattering, factors given by these programs. Structure solved by Patterson function and heavy-atom method and refined on F by a full-matrix least-squares method with anisotropic thermal motion. $(\Delta/\sigma)_{max} = 0\cdot004$, $\Delta\rho \le 3$ e Å^{-3}, $R = 0\cdot029$, $wR = 0\cdot033$, $S = 1\cdot3$, $w = 1/\sigma^2(F)$. Atomic parameters in Table 1.*

The structure of $K_{0\cdot75}MoNbP_3O_{12}$ is very similar to those described for the pure molybdenum phosphates $AMo_2P_3O_{12}$ (A = K, Rb, Tl) (Leclaire *et al.*, 1983; Leclaire & Raveau, 1988) or for the molybdenum tungsten phosphate $KMoWP_3O_{12}$ (Benmoussa, Leclaire, Grandin & Raveau, 1989). The host lattice $[MoNbP_3O_{12})$ (Fig. 1) is indeed built up from MoO_6 and NbO_6 octahedra and PO_4 tetrahedra which form tunnels running along **b**, where the potassium ions are located. The simultaneous presence of PO_4 and P_2O_7 groups allows the formula $K_{0\cdot75}MoNbO(PO_4)(P_2O_7)$ or $K_3Mo_4Nb_4O_4(PO_4)_4$-$(P_2O_7)_4$ or $K_3Mo_4Nb_4P_{12}O_{48}$ to be proposed.

The original feature concerns the occupancy factor of the potassium sites which was refined to 0·75, with a statistical distribution of these cations in the tunnels. This result is also confirmed by the fact that the oxide $K_{0\cdot75}MoNbP_3O_{12}$ can be synthetized as a powder in a quantitative way, whereas the oxide $KMoNbP_3O_{12}$ cannot be obtained as a pure phase. This shows the ability of this structure to show a significant deviation from stoichiometry for the K^+ ions.

Like $KMoWP_3O_{12}$ and contrary to $KMo_2P_3O_{12}$, this phase does not exhibit a superstructure along **a**.

The $P(1)O_4$ tetrahedra which are only linked to MoO_6 and NbO_6 octahedra are very regular, with P—O distances ranging from 1·519 to 1·520 Å (Table 2); on the other hand, the $P(2)O_4$ tetrahedra which belong to the P_2O_7 groups have one long P—O bond of 1·601 Å corresponding to the bridging oxygen of the diphosphate group and three other P—O distances ranging from 1·503 to 1·507 Å.

The Mo and Nb atoms are distributed at random on one equivalent site as in $KMoWP_3P_{12}$, leading to only one type of octahedron, $(MoNb)O_6$. The geometry of these octahedra is very similar to that observed for $KMo_2P_3O_{12}$: one observes one shorter metal–oxygen distance of 1·908 Å (Table 2) which corresponds to the O atom common to two octahedra and five longer metal–oxygen distances, ranging from 2·004 to 2·105 Å.

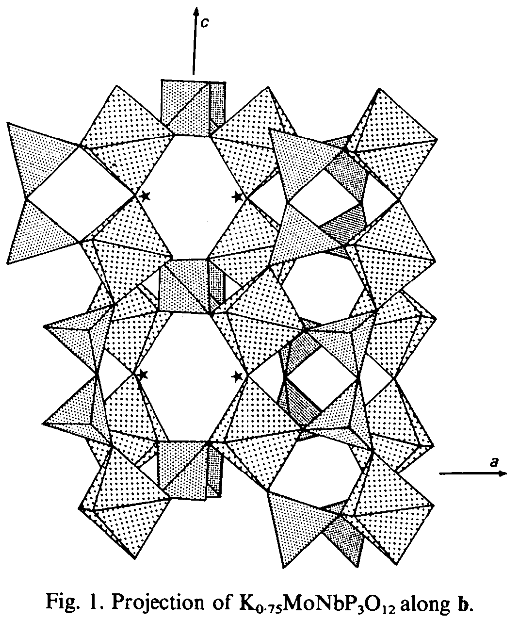

Fig. 1. Projection of $K_{0\cdot75}MoNbP_3O_{12}$ along **b**.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52854 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Distances* (Å) *and angles* (°)

PO_4 tetrahedra

P(1)	O(2^{i})	O(2^{ii})	O(6)	O(6^{iii})
O(2^{i})	1·519 (5)	2·486 (7)	2·490 (6)	2·438 (6)
O(2^{ii})	109·8 (3)	1·519 (5)	2·438 (6)	2·490 (6)
O(6)	110·1 (2)	106·7 (2)	1·520 (4)	2·543 (6)
O(6^{iii})	106·7 (2)	110·1 (2)	113·5 (2)	1·520 (4)

P(2)	O(3^{iii})	O(4)	O(5^{iv})	O(7)
O(3^{iii})	1·507 (5)	2·534 (6)	2·543 (6)	2·422 (5)
O(4)	114·7 (3)	1·503 (4)	2·443 (6)	2·506 (7)
O(5^{iv})	115·2 (3)	108·6 (3)	1·506 (4)	2·509 (6)
O(7)	102·3 (3)	107·7 (3)	107·7 (3)	1·601 (3)

$MoNbO_6$ octahedra

MoNb	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1·908 (1)	2·816 (6)	4·012 (7)	2·814 (7)	2·778 (6)	2·832 (6)
O(2)	92·1	2·004 (5)	2·902 (6)	4·031 (7)	2·805 (6)	2·884 (6)
O(3)	177·7 (2)	89·8 (2)	2·105 (4)	2·843 (6)	2·886 (6)	2·889 (6)
O(4)	91·2 (2)	176·0 (2)	86·9 (2)	2·030 (4)	2·846 (6)	2·875 (6)
O(5)	90·0 (2)	88·4 (2)	88·8 (2)	89·3 (2)	2·020 (4)	4·036 (7)
O(6)	92·3 (2)	91·7 (2)	89·0 (2)	90·5 (2)	177·7 (2)	2·017 (4)

KO_8 polyhedra

K—O(7^{v})	2·753 (8)	K—O(6^{vii})	3·042 (6)
K—O(2^{ii})	2·825 (6)	K—O(3^{i})	3·187 (6)
K—O(2^{vi})	2·825 (6)	K—O(3^{viii})	3·187 (6)
K—O(6)	3·042 (6)	K—O(1^{ii})	3·278 (8)

Symmetry code: (i) $-x, -y, -z$; (ii) $-x, 0·5+y, z$; (iii) $x, 0·5-y, -z$; (iv) $1-x, 0·5+y, z$; (v) $-x, y-0·5, z$; (vi) $-x, 0·5-y, 0·5-z$; (vii) $x, y, 0·5-z$; (viii) $-x, -y, 0·5+z$.

The K ions are surrounded by eight O atoms, with distances less than 3·35 Å (Table 2).

It is worth pointing out that the metallic elements in octahedral coordinations exhibit a mean oxidation state of 4·125 compared with 4 for $KMo_2P_3O_{12}$. Because of the difficulty of niobium being in the tetravalent state in phosphates, unlike molybdenum which can be presumed to be Mo^{IV}, a mean valency of 4·25 is suggested for niobium which coincides with that observed in $Na_{0·5}Nb_2P_3O_{12}$ (Leclaire *et al.*, 1990).

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Structure of Barium Copper Pyrosilicate at 300 K

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Abstract. Barium dicopper disilicate, $BaCu_2Si_2O_7$, M_r = 432·6, orthorhombic, $Pnma$, $a = 6·866$ (2), $b =$ 13·190 (3), $c = 6·909$ (2) Å, $V = 625·7$ (3) Å^3, $Z = 4$, $D_x = 4·592$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu =$ 137·47 cm^{-1}, $F(000) = 792$, $T = 300$ K, final $R =$ 0·031 for 1039 independent reflections. The structure solution and refinement established the crystal stoichiometry as $BaCu_2Si_2O_7$. The structure contains isolated groups of $[Si_2O_7]^{6-}$ with the Si—O distances ranging from 1·610 (4) to 1·662 (2) Å. The barium and copper cations have irregular coordination polyhedra. Ba^{2+} is coordinated by 7 O atoms, and Cu^{2+} by 4 + 1 O atoms.

Introduction. The '1-2-3'-type superconductors have the ability to interact with oxygen. This interaction is very important because superconducting properties depend on the oxygen stoichiometry (Pietraszko,

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