A Mixed Valent Titanium Diphosphate with an Intersecting Tunnel Structure: $K_{0.58}TiP_2O_7$

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A new mixed valent titanium diphosphate $K_{0.58}TiP_2O_7$, has been isolated. It crystallizes in the space group $C2/c$ with $a = 17.852$ (2) Å, $b = 6.298$ (1) Å, $c = 12.181$ (2) Å, $\beta = 119.73$ (1)°. Its $[TiP_2O_7]_\infty$ framework consists of corner-sharing TiO_6 octahedra and P_2O_7 groups forming tunnels running along [010], [001], and [101]. This structure can be described either from TiP_2O_{11} units characteristic of many diphosphates $A_xMP_2O_7$, or from $[TiPO_8]_\infty$ encountered in many monophosphates. The K^+ ions are distributed over two kinds of sites, K(1) with a flattened octahedral coordination, and K(2) with a strongly distorted cubic coordination. The low occupancy of the second kind of site (16%) suggests the possibility of a wide of nonstoichiometry. © 1994 Academic Press, Inc.

INTRODUCTION

A large series of diphosphates of transition elements with the generic formula AMP_2O_7 has been isolated over the past ten years. The first family obtained for A = Na and M = V(III) (1), Mo(III) (2), and Ti(III) (3) exhibits the $NaAlP_2O_7$ structure (4), whereas the second large family, synthesized for A = K, M = Mo(III) (5), V(III) (6), and Ti(III) (7), for A = Rb, M = Mo(III) (8), V(III) (9), and Ti(III) (7), and for A = Cs, M = Mo(III) (10), Ti(III) (7), and V(III) (11) is isotypic of $KAlP_2O_7$ (12). On the contrary, very few diphosphates with a cation deficiency, i.e., with the formula $A_{1-x}MP_2O_7$, are actually known. Aside from the diphosphates $BaM_2P_4O_{14}$ (M = Ti(III), V(III), and Mo(III)) (13–15) there exist only two cationic deficient diphosphates, $Na_xMoP_2O_7$ (16, 17) and $K_{0.17}MoP_2O_7$ (5), that are characterized by a mixed valence of molybdenum Mo(III)–Mo(IV). In order to test the ability of titanium to form similar mixed valent diphosphates we have investigated the compositions $K_{1-x}TiP_2O_7$. The present paper deals with a new diphosphate $K_{0.58}TiP_2O_7$ with an original structure.

SYNTHESIS

Single crystals of this new phosphate were grown from a mixture of nominal composition $K_{0.3}TiP_2O_7$.

The synthesis was performed in two steps: first an adequate mixture of K_2CO_3, $H(NH_4)_2PO_4$, and TiO_2 was ground and heated to 673 K in air to eliminate CO_2, H_2O, and NH_3. In a second step, the appropriate amount of titanium was added and the finely ground mixture was placed in an alumina tube and sealed in an evacuated silica tube, then heated for 1 day to 1273 K and cooled at 2 K h^{-1} to 1073 K. The sample was finally quenched to room temperature. In the mixture, some dark blue crystals were extracted. The microprobe analysis of these crystals confirms the composition $K_{0.58}TiP_2O_7$, in agreement with the structure determination.

The attempts to obtain a pure phase failed; only mixtures are obtained.

STRUCTURE DETERMINATION

A blue crystal with dimensions $0.077 \times 0.064 \times 0.045$ mm was selected for structure determination. The cell parameters reported in Table 1 were determined by diffractometric techniques at 294 K with a least-squares refinement based upon 25 reflections with $18° \leq \theta \leq 22°$. The data were collected on a CAD 4 Enraf–Nonius diffractometer with the data collection parameters reported in Table 1. The reflections were corrected for Lorentz and polarization effects. No absorption corrections were performed.

The structure was solved by the heavy atom method. The Patterson function allowed the Ti atom to be located; then the phosphorus, oxygen, and K(1) atoms were found with subsequent Fourier synthesis. After refinement of these atomic parameters, the value of the R and R_w factors were 0.057 and 0.064, respectively. The Fourier synthesis showed a residual peak at 0.0, 0.105, 0.25 corresponding to small amount of potassium K(2).

The final refinement of the K(2) occupancy leads to the formula $K_{0.58}TiP_2O_7$, with R = 0.052 and R_w = 0.060 for the atomic parameters given in Table 2.

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TABLE 1

Summary of Crystal Data Intensity, Measurements, and
Structure Refinement Parameters for $K_{0.58}TiP_2O_7$

1 Crystal data
Space group	$C2/c$
Cell dimensions	$a = 17.852$ (2) Å
	$b = 6.298$ (1) Å, $\beta = 119.73$ (1)°
	$c = 12.181$ (2) Å
Volume	1189 (7) Å³
Z	8

2 Intensity measurements
$\lambda(MoK\alpha)$	0.71073
Scan mode	$\omega - 4/3\ \theta$
Scan width (°)	$1.40 + 0.35 \tan \theta$
Slit aperture (mm)	$1.30 + \tan \theta$
Max θ(°)	45
Standard reflections	3 (every 3000 sec)
Reflections with $I > 3\sigma$	697
μ (mm⁻¹)	2.29

3 Structure solution and refinement
Parameters refined	103
Agreement factors	$R = 0.052$, $R_w = 0.060$
Weighting scheme	$w = f(\sin \theta/\lambda)$
Δ/σ max	<0.004
$\Delta\sigma\ (e\text{Å}^{-3})$	<0.5

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Projection of the structure of $K_{0.58}TiP_2O_7$ onto the (010) plane (Fig. 1) shows that its framework $[TiP_2O_7]_\infty$ consists of corner-sharing diphosphate groups and TiO_6 octahedra. It is characterized by the existence of TiP_2O_{11} units

TABLE 2

Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	$B(\text{Å}^2)$
Ti	0.36879(9)	0.1029(4)	0.2804(1)	0.53(2)
P(1)	0.4133(1)	0.1114(5)	0.0463(2)	0.54(3)
P(2)	0.1534(1)	0.1155(5)	0.1686(2)	0.56(3)
K(1)[a]	0.2701(4)	0.331(2)	0.5091(5)	6.1(2)
K(2)[a]	0.	0.11(1)	0.25	4.9(8)[b]
O(1)	0.2443(4)	0.112(2)	0.1881(6)	1.7(1)
O(2)	0.3593(4)	−0.210(1)	0.2553(5)	0.9(1)
O(3)	0.3648(4)	0.141(2)	0.1177(5)	1.2(1)
O(4)	0.4931(4)	0.068(1)	0.3683(5)	0.9(1)
O(5)	0.3775(4)	0.408(2)	0.3101(6)	1.3(1)
O(6)	0.3688(4)	0.056(1)	0.4442(6)	1.0(1)
O(7)	0.0923(4)	0.167(1)	0.0220(6)	1.0(1)

Note. Anisotropically refined atoms are given in the isotropic equivalent displacement parameter defined as $B = 4/3\ [\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}\ c^2 + \beta_{12}\ ab \cos \gamma + \beta_{13}ac \cos \beta + \beta_{23}bc \cos \alpha]$.

[a] Multiplicity of K(1) = 0.5; multiplicity of K(2) = 0.08(1).
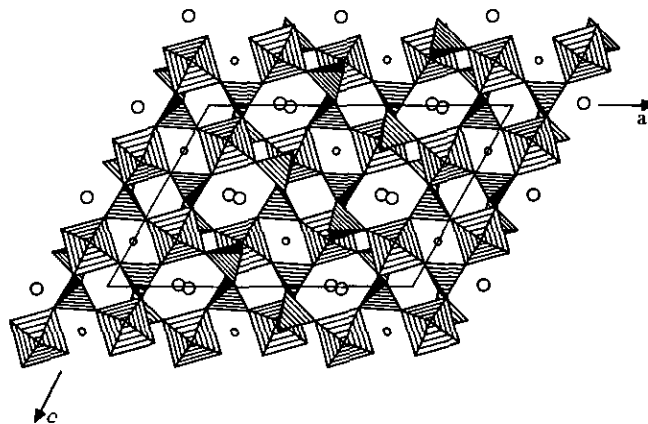
[b] Refined isotropically.

FIG. 1. Projection of the structure of $K_{0.58}TiP_2O_7$ onto the (010) plane.

built from one P_2O_7 group sharing two opposite corners with the same TiO_6 octahedron. Such units seem to be characteristic of many diphosphates of transition elements with the generic formula $A_xMP_2O_7$. It is indeed observed for all the stoichiometric diphosphates $NaMP_2O_7$ with $M =$ Fe, Mo, Ti (18, 2, 3), $LiMP_2O_7$ with $M =$ Fe, Ti (19, 20), KMP_2O_7 with $M =$ Fe, Mo, Ti (21, 5, 7), $RbMP_2O_7$ with $M =$ Mo, Ti (8, 7), and $CsMP_2O_7$ with $M =$ Mo, Ti (10, 7), but also in the nonstoichiometric diphosphate $K_{0.17}MoP_2O_7$ (5). This tendency to form such units is also recognized in the diphosphates $BaTi_2(P_2O_7)_2$ (13) and $Na_xMoP_2O_7$ (16, 17), but in these structures two diphosphate groups are connected in the same way on two opposite edges of the same octahedron.

Thus the whole $[TiP_2O_7]_\infty$ framework can be described from the assemblage of such TiP_2O_{11} units. Along $\vec{b}$, two TiP_2O_{11} share the corners of their polyhedra in such a
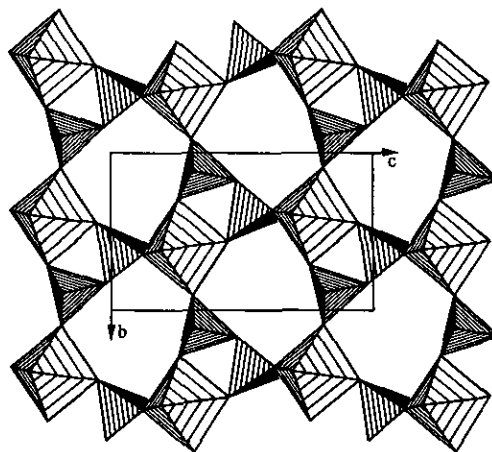

FIG. 2. $[Ti_2P_4O_{18}]$ layers characterized by large six-sided windows and $[TiP_2O_{10}]_\infty$ chain.

way that one P_2O_7 group of one unit is linked to the TiO_6 octahedron of the next unit, forming $[TiP_2O_{10}]_\infty$ chains (Fig. 2). Laterally, in the (100) plane, the $[TiP_2O_{10}]_\infty$ chains share the corners of their polyhedra, so that they form $[Ti_2P_4O_{18}]_\infty$ layers characterized by large six-sided windows (Fig. 2). Along $\bar{a}$, the $[Ti_2P_4O_{18}]_\infty$ mixed layers share the corners of their polyhedra. Therefore the $[TiP_2O_7]_\infty$ framework can be described as the regular stacking of identical $[Ti_2P_4O_{18}]_\infty$ layers along $\bar{a}$, as shown from the projections of the structure along $\bar{b}$ (Fig. 1) and along $\bar{c}$ (Fig. 3).

Another description of the structure can be given by considering the chains of polyhedra running along $\bar{c}$ on the (010) projection (Fig. 1). One indeed recognizes $[TiPO_8]_\infty$ chains in which one TiO_6 octahedron alternates with a first kind of PO_4 tetrahedron labeled $P(1)$ (Fig. 4). Such chains are classically observed in many phosphates of transition elements (22). In the $[TiPO_8]_\infty$ chains the PO_4 tetrahedra point above and below the basal plane of the TiO_6 octahedron alternately. The $[TiPO_8]_\infty$ chains form double $[Ti_2P_2O_{14}]_\infty$ chains running along $\bar{c}$ (Fig. 4) by sharing the corners of their polyhedra in such a way that one PO_4 tetrahedron of one chain is connected with the TiO_6 octahedron of the other chain. Several phosphates of transition metals exhibit this mode of linking, especially monophosphates. However, in $K_{0.58}TiP_2O_7$, the double $[Ti_2P_2O_{14}]_\infty$ chains are linked to each other, through a second kind of PO_4 tetrahedron labeled $P(2)$ along $\bar{a}$ (Fig. 1) and along $\bar{b}$ (Fig. 3). The $P(2)$ tetrahedra share one corner with one octahedron of one chain and two other corners with one octahedron and one tetrahedron ($P(1)$ of the other chain). As a result one obtains diphosphate groups involving two independent tetrahedra $P(1)$ and $P(2)$, which form the TiP_2O_{11} units described above.

The $[TiP_2O_7]_\infty$ framework delimits rather large six-

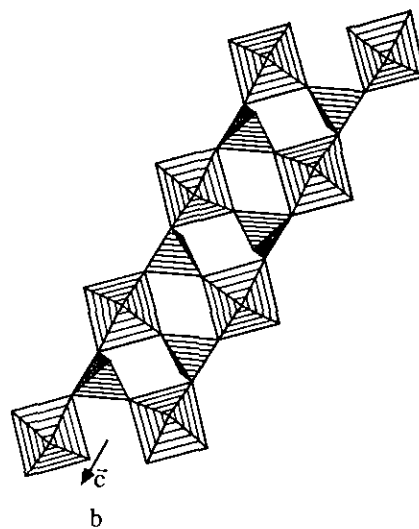FIG. 4. $[Ti_2P_2O_{14}]$ double chain formed by two corner-sharing $[TiPO_8]_\infty$ chains.

sided tunnels running along $\bar{b}$ (Fig. 1) and along $\bar{c}$ (Fig. 3), respectively, where the potassium ions are located. Despite their different directions these tunnels do not intersect. In addition to these large, well-defined tunnels, this framework exhibits "zig-zag" tunnels running along [101] (Fig. 5) which intersect both six-sided tunnels running along $\bar{b}$ and $\bar{c}$, respectively. Thus $K_{0.58}TiP_2O_7$ can be considered to be characterized by an intersecting tunnel structure.

In this structure, each TiO_6 octahedron shares its six corners with six PO_4 tetrahedra. Consequently its geometry is almost regular, with Ti–O distances ranging from 1.930 to 2.015 Å (Table 3). The electrostatic valence calculation according to Brese and O'Keeffe (23) leads, for titanium, to a mean valence of 3.67, in agreement with that deduced from the chemical formula (3.42). Taking
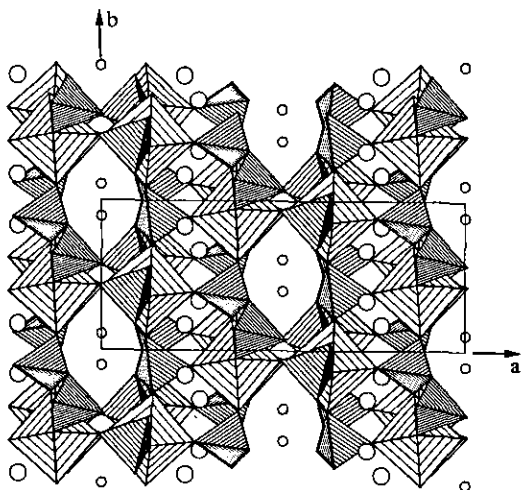

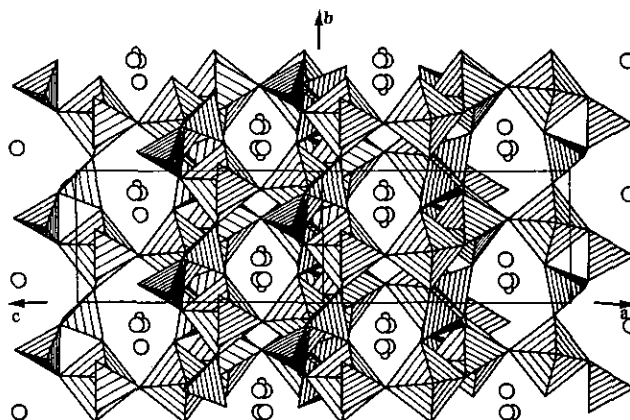FIG. 3. Projection of the structure of $K_{0.58}TiP_2O_7$ along $\bar{c}$.

FIG. 5. Projection along [101].

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TABLE 3
Distances (Å) and Angles (°) in the Polyhedra

Ti	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1.930(8)	2.71(2)	2.69(1)	3.86(2)	2.80(1)	2.81(1)
O(2)	87.4(5)	1.99(1)	2.80(1)	2.72(1)	3.93(2)	2.78(1)
O(3)	87.3(3)	90.5(4)	1.963(8)	2.80(1)	2.80(1)	3.98(1)
O(4)	175.0(5)	87.7(4)	91.7(3)	1.939(8)	2.80(1)	2.79(1)
O(5)	92.3(5)	178.0(4)	91.4(4)	92.6(4)	1.94(1)	2.80(1)
O(6)	91.0(4)	88.0(4)	177.7(4)	89.9(3)	90.1(4)	2.015(8)

P(1)	O(3)	O(4^i)	O(6^{ii})	O(7^{iii})
O(3)	1.512(7)	2.50(1)	2.48(1)	2.49(1)
O(4^i)	112.5(4)	1.489(7)	2.51(1)	2.48(1)
O(6^{ii})	110.0(5)	113.3(5)	1.517(9)	2.52(1)
O(7^{iii})	106.4(6)	106.4(5)	107.8(5)	1.601(9)

P(2)	O(1)	O(2^{iv})	O(5^v)	O(7)
O(1)	1.518(8)	2.53(1)	2.53(1)	2.47(1)
O(2^{iv})	112.6(6)	1.526(9)	2.48(1)	2.53(1)
O(5^v)	114.8(7)	110.3(5)	1.492(9)	2.46(1)
O(7)	105.2(5)	107.9(5)	105.5(5)	1.597(8)

		K(2) –	O(2^{viii}) = 2.80(3)
K(1) –	O(1^{iv}) = 2.89(1)	K(2) –	O(2^{iv}) = 2.80(3)
K(1) –	O(2^{ii}) = 2.72(1)	K(2) –	O(4^{viii}) = 3.28(6)
K(1) –	O(2^{iv}) = 2.90(1)	K(2) –	O(4^{iv}) = 3.28(6)
K(1) –	O(3^{iv}) = 2.88(1)	K(2) –	O(5^{ix}) = 2.91(3)
K(1) –	O(3) = 2.85(1)	K(2) –	O(5^v) = 2.91(3)
K(1) –	O(6^{viii}) = 2.89(1)	K(2) –	O(7^x) = 3.35(4)
		K(2) –	O(7^{vi}) = 3.35(4)

Symmetry Code

i	$1 - x$	y	$1/2 - z$
ii	x	$-y$	$-1/2 + z$
iii	$1/2 - x$	$1/2 - y$	$-z$
iv	$1/2 - x$	$1/2 + y$	$1/2 - z$
v	$1/2 - x$	$-1/2 + y$	$1/2 - z$
vi	x	$-y$	$1/2 + z$
vii	$1/2 - x$	$1/2 - y$	$1 - z$
viii	$-1/2 + x$	$1/2 + y$	z
ix	$-1/2 + x$	$-1/2 + y$	z
x	$-x$	$-y$	$-z$

into account the fact that the TiO$_6$ octahedra are isolated, this suggests that Ti(III) and Ti(IV) species are distributed statistically in the octahedral sites.

Each P$_2$O$_7$ group is built up from one P(1) and one P(2) tetrahedron, and shares its other six corners with five TiO$_6$ octahedra. Its configuration is intermediate between the staggered configuration of KTiP$_2$O$_7$ (7) and the eclipsed configuration of NaTiP$_2$O$_7$ (3). In both P(1) and P(2) groups, the P–O bonds are characteristic of the P$_2$O$_7$ groups, i.e., for each group, one long P–O distance (1.597–1.601 Å) corresponding to the bridging oxygen and three shorter P–O distances (1.489–1.526 Å) corresponding to the oxygen atoms shared with TiO$_6$ octahedra.

The K(1) atom is located at the crossing of the [010] and [101] tunnels. It is offcentered in the cage, forming a flattened octahedron with K–O distances ranging from 2.72 to 2.90 Å (Table 3). In fact K(1) is distributed over two sites that are located within the same cage but on both sides of the symmetry center; the latter are only half-occupied owing to their too-short distance (1.2 Å).

The second atom, K(2), is located at the crossing of the [001] and [101] tunnels. It exhibits a very distorted cubic coordination, with K–O distances spreading over a much wider range (2.80 to 3.35 Å). One interesting feature deals with the low occupancy of this site, only 16%, which suggests a large possibility of nonstoichiometry in this structure.

CONCLUDING REMARKS

This study confirms the great ability of $[MP_2O_7]_\infty$ frameworks to form MP_2O_{11} units. The existence of intersecting tunnels suggests the possibility of ionic mobility. The open character of this structure favors a wide range of nonstoichiometry whose study is in progress.

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