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$K_{2-x}Ti_2(PO_4)_3$ with $0 \leq x \leq 0.5$: A Mixed-Valence Nonstoichiometric Titanophosphate with the Langbeinite Structure

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A new nonstoichiometric titanophosphate, $K_{2-x}Ti_2(PO_4)_3$, has been isolated for $0 \leq x \leq 0.5$. This compound which belongs to the Langbeinite structure is characterized by a mixed valence of titanium Ti^{III}/Ti^{IV}. The structures of two compositions $x = 0$ and $x = 0.25$ have been determined from a single-crystal X-ray diffraction study. This cubic phase ($a = 9.8559$ Å for $x = 0.25$, $a = 9.8688$ Å for $x = 0$; space group $P2_13$) is compared to Nasicon $Na_xTi_2(PO_4)_3$. The evolution of the Ti–O distances and calculations of the mean oxidation state of titanium allow a distribution of the Ti^{III} and Ti^{IV} ions on the two types of site to be proposed. The possibility of extending this structure to other univalent cations has been demonstrated with the synthesis of the isotypic compounds $Rb_2Ti_2(PO_4)_3$ and $Tl_2Ti_2(PO_4)_3$.

Introduction

The introduction of mixed-valence cations in oxides characterized by a mixed framework of octahedra and tetrahedra can be used to generate particular physical properties. This is the case in the large family of phosphate tungsten bronzes, in which the mixed valence W^V–W^{VI} induces a total delocalization of the electrons leading to the existence of an anisotropic metallic conductivity (see, for review, Ref. (*1*)). More recently, two molybdenum compounds with a mixed valence of molybdenum Mo^{III}–Mo^{IV} were isolated: the silicophosphate $KMo_3P_6Si_2O_{25}$ (*2*) and the molybdenophosphate $Na_{0.3}MoP_2O_7$ (*3*). In these latter oxides, the MoO_6 octahedra are isolated from each other so that a delocalization of the electrons is not possible. This raises the questions of the ordering of the eventual Mo^{III} and Mo^{VI} ions in the structure, or the possibility of the existence of intermediate valence states between III and IV. Few frameworks involving the mixed valence Ti^{III}–Ti^{IV} are known at the present time despite the ability of titanium to present such a behavior in pure octahedral structures. The well-known Nasicon phosphate $Na_xTi_2(PO_4)_3$ isolated by Nadiri (*4*) is one of the rare mixed-valence titanium phosphates. These compositions exhibit a large deviation from stoichiometry, with x ranging from 1 to 3.

No electronic delocalization can be observed because of the fact that the TiO_6 octahedra are isolated. Moreover, the problem of the distribution of the tetravalent and trivalent ions in the structure is not yet understood. We report here on the synthe-

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sis and structural study of a new mixed-valence titanophosphate: $K_{2-x}Ti_2(PO_4)_3$ belonging to the Langbeinite structure (*5*).

Synthesis and Homogeneity Range

The different compositions $K_{2-x}Ti_2(PO_4)_3$ were prepared in the following way: K_2CO_3, $H(NH_4)_2PO_4$ and TiO_2 were first mixed in an agate mortar in ratios to reach the exact ratio of four oxygen atoms per phosphorus according to the final formula. The mixtures were first heated in air at 350°C for decarbonation and deamination. The resulting products were mixed with an adequate amount of metallic titanium, placed in alumina crucibles, and heated in evacuated silica ampoules at temperatures ranging from 1100 to 1200°C. Under these conditions a pure phase was isolated for x ranging from 0 to 0.5. The X-ray diffractograms of the different compositions are characteristic of the Langbeinite-type structure and are indexed in the cubic system. The cubic cell parameter increases from $a = 9.850$ Å for $x = 0.5$ to $a = 9.866$ Å for $x = 0$, in agreement with the increasing content of potassium, and the progressive replacement of Ti^{IV} by Ti^{III}. The color of the samples ranges from light blue to dark blue as x decreases from 0.5 to 0 in agreement with the mixed-valence titanium.

In this method of synthesis, single crystals could be isolated from the bulk. Two dark blue single crystals with formulas $K_{1.75}Ti_2(PO_4)_3$ and $K_2Ti_2(PO_4)_3$ were selected for structure determination.

Isotypic Compounds

Attempts to prepare the rubidium and thallium isotypic oxides were successful. $Rb_2Ti_2(PO_4)_3$ and $Tl_2Ti_2(PO_4)_3$ could indeed be prepared as pure phases using similar experimental conditions. These oxides were only identified from their X-ray powder diffractograms $CuK\alpha$ radiation. No attempt was made to grow single crystals. The parameters of the cubic cell are very similar for both compounds and greater than that of potassium in agreement with the size of the univalents: $a = 9.9115$ Å for $Rb_2Ti_2(PO_4)_3$, $a = 9.9386$ Å for $Tl_2Ti_2(PO_4)_3$.

Determination of the Structure

The two crystals selected for the structure determination had the following dimensions: 0.096 × 0.072 × 0.026 mm for $K_{1.75}Ti_2(PO_4)_3$ and 0.12 × 0.096 × 0.072 for $K_2Ti_2(PO_4)_3$. In both cases the diffraction patterns showed a cubic symmetry and the systematic absences led to the $P2_13$ space group characteristic of Langbeinite (*5*). The cell parameters initially measured in Weissenberg films and later refined by diffractometric techniques at 294 K with least-squares refinements based on 25 reflections are

$$a = 9.8559(6)\ \text{Å} \quad \text{for } K_{1.75}Ti_2(PO_4)_3$$

$$a = 9.8688(6)\ \text{Å} \quad \text{for } K_2Ti_2(PO_4)_3$$

with $Z = 4$ formula units $K_{2-x}Ti_2(PO_4)_3$. The data were collected on a CAD-4 Enraf–Nonius diffractometer with $MoK\alpha$ radiation ($\lambda = 0.71069$ Å). The intensities were measured up to $\theta = 45°$ with a $\omega - \theta$ scan of $(0.8 + 0.35 \tan \theta)°$ and a counterslit aperture of $(1 + \tan \theta)$ mm, all determined after a study of some reflections in the $\omega - \theta$ plane. The background intensity was measured on both sides of each reflection. A periodic measurement of three reflections verified the stability of the sample. Three hundred sixty-three and 743 independent reflections with $I \geq 3\sigma(I)$ were corrected for Lorentz and polarization effects for $K_{1.75}Ti_2(PO_4)_3$ and $K_2Ti_2(PO_4)_3$, respectively. No absorption corrections were made. The two positions of titanium and the two positions of potassium were deduced from the Patterson function in both cases. The positions of the other atoms were deduced from subsequent Fourier series. Refinement of the atomic parameters and isotropic thermal factors led to $R =$

0.046 and $R_w = 0.055$ for $K_{1.75}Ti_2(PO_4)_3$, considering a full occupancy of the potassium sites, whereas the discrepancy factors were lowered to $R = 0.03$ and $R_w = 0.04$ for $K_2Ti_2(PO_4)_3$. At this stage the main difference between the two crystals dealt with a high thermal factor for (K2) observed for $K_{1.75}Ti_2(PO_4)_3$ (B(K1) = 1.55 and B(K2) = 2.31), contrary to $K_2Ti_2(PO_4)_3$ which exhibited correct B factors (B(K1) = 1.65 and B(K2) = 1.73). These observations suggested that the occupancy factor of K2 should be smaller than 1 for $K_{1.75}Ti_2(PO_4)_3$. Refinements of the atomic parameters, of the anisotropic thermal factors, and of the occupancy of the potassium sites confirmed this. The discrepancy factors were lowered to $R = 0.036$ and $R_w = 0.041$ for the atomic parameters given in Table I in the case of $K_{1.75}Ti_2(PO_4)_3$, whereas no significant variation was observed in the case of $K_2Ti_2(PO_4)_3$, atomic parameters of which are given in Table II. It can be seen that the B_{eq} values of the potassium ions are close for both crystals but that the occupancy factors of those sites remain equal to 1 in the case of $K_2Ti_2(PO_4)_3$ while the occupancy of the K2 sites is lowered to 0.75 for $K_{1.75}Ti_2(PO_4)_3$ in agreement with this latter formula deduced from microprobe analysis.

Description of the Structure and Discussion

The Langbeinite framework (Fig. 1) contains isolated PO_4 tetrahedron, each sharing its four corners with a TiO_6 octahedron. Reciprocally the TiO_6 octahedra are isolated; each octahedron is linked to six PO_4 tetrahedra. This structure exhibits some similarities with that of Nasicon (Fig. 2). Both mixed frameworks are built up from similar $[Ti_2P_3O_{18}]$ structural units (Fig. 3) composed of two TiO_6 octahedra linked to each other through three PO_4 tetrahedra. The difference between the two structures concerns the arrangement of these structural units. In the Langbeinite structure, eight of these units share the corners of their polyhedra in such a way that they form large cages in which the potassium is located. Moreover, along the ternary axis of such units one observes a sequence of $[Ti_2P_3O_{18}]$ units separated by two K^+ ions. In Nasicon, the ternary axes of these units are all parallel so that eight units define a smaller cavity than in Langeinite. On the other hand, the windows formed by these units are much smaller in Langbeinite than in Nasicon. Consequently, Langbeinite is a true cage structure whereas Nasicon is characterized by zigzag tunnels which are responsible for the fast Na^+ ionic conductivity.

TABLE I

ATOM PARAMETERS FOR $K_{1.75}Ti_2(PO_4)_3$

Atom	x	y	z	B_{eq}
Ti1	0.58721(16)	0.58721(16)	0.58721(16)	0.41(2)
Ti2	0.85809(17)	0.85809(17)	0.85809(17)	0.43(2)
K1	0.29175(27)	0.29175(27)	0.29175(27)	1.65(5)
K2	0.06618(29)	0.06618(29)	0.06618(29)	1.16(6)
P	0.27407(25)	−0.37213(25)	0.45889(24)	0.44(4)
O1	0.00066(65)	0.07490(71)	0.35238(77)	0.97(13)
O2	0.26636(78)	−0.42225(81)	0.31360(67)	1.02(13)
O3	0.47087(72)	0.05361(69)	0.29809(75)	1.14(15)
O4	0.20400(72)	−0.23500(71)	0.47771(75)	1.04(14)

The results show clearly the ability of the Langbeinite structure to become nonstoichiometric. In this respect attention must be drawn to the oxide $KTi_2(PO_4)_3$, the structure of which was determined by Masse *et al.* (*6*) several years ago. This oxide, which corresponds to the lower limit of the series

TABLE II

ATOM PARAMETERS FOR $K_2Ti_2(PO_4)_3$

Atom	x	y	z	B_{eq}
Ti1	0.66257(8)	0.66257(8)	0.66257(8)	0.34(0)
Ti2	0.39258(8)	0.39258(8)	0.39258(8)	0.38(0)
K1	0.95591(15)	0.95591(15)	0.95591(15)	1.65(2)
K2	0.18437(14)	0.18437(14)	0.18437(14)	1.73(2)
P	0.47556(12)	0.70937(12)	0.37811(12)	0.41(1)
O1	0.60215(40)	0.82705(39)	0.75011(38)	0.91(6)
O2	0.45286(40)	0.30460(40)	0.21980(39)	1.10(6)
O3	0.48428(41)	0.56425(38)	0.32696(41)	0.95(6)
O4	0.54510(42)	0.72680(42)	0.51655(38)	1.15(7)

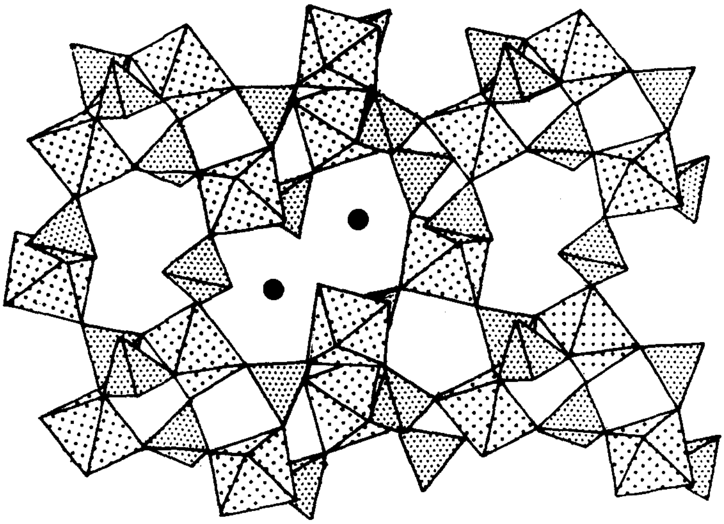

FIG. 1. Partial projection of the $K_{2-x}Ti_2(PO_4)_3$ showing the cages where the K atoms lie.

and which would involve only Ti^{IV}, could not be synthesized here. Moreover, it is worth pointing out that these authors could only get "some" single crystals in the melt.

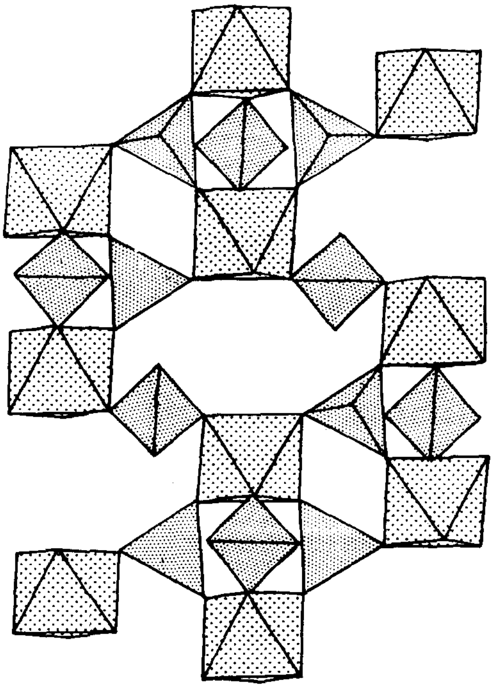

FIG. 2. Partial projection of the Nasicon structure.

The blue color of their crystals suggest that some Ti^{III} should be present, leading to a limit slightly different from $x = 1$, and not detectable from the X-ray diffraction determination.

The evolution of the interatomic distances versus composition is remarkable. One observes that the four P–O bonds of the tetrahedra are almost equal and do not vary within the limits of the standard deviations (Table III), in agreement with the fact that the PO_4 tetrahedra are isolated. On the other hand the Ti–O distances increase as x

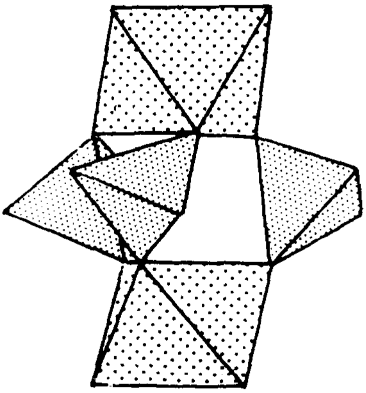

FIG. 3. The $Ti_2P_3O_{18}$ unit common to the Nasicon and Langbeinite structures.

TABLE III

MAIN BOND LENGTHS

$K_{1.75}Ti_2(PO_4)_3$	$K_2Ti_2(PO_4)_3$
Ti1–O1 = 1.907(7) Å ×3	Ti1–O1 = 1.933(4) Å ×3
Ti1–O4 = 1.964(7) Å ×3	Ti1–O4 = 1.955(4) Å ×3
Ti2–O3 = 1.987(7) Å ×3	Ti2–O2 = 2.027(4) Å ×3
Ti2–O2 = 2.020(7) Å ×3	Ti2–O3 = 2.027(4) Å ×3
P–O1 = 1.557(7) Å	P–O1 = 1.532(4) Å
P–O2 = 1.517(7) Å	P–O2 = 1.522(4) Å
P–O3 = 1.525(7) Å	P–O3 = 1.521(4) Å
P–O4 = 1.529(7) Å	P–O4 = 1.539(4) Å
K1–O2 = 2.838(8) Å ×3	K1–O3 = 2.813(4) Å ×3
K1–O3 = 2.938(7) Å ×3	K1–O2 = 2.932(4) Å ×3
K1–O4 = 3.145(8) Å ×3	K1–O4 = 3.188(4) Å ×3
K2–O1 = 2.895(8) Å ×3	K2–O1 = 2.902(4) Å ×3
K2–O3 = 2.917(8) Å ×3	K2–O2 = 2.924(4) Å ×3
K2–O4 = 2.943(8) Å ×3	K2–O3 = 2.939(4) Å ×3

decreases (Table III), in agreement with the fact that the mean oxidation state of titanium decreases. It can be seen that the TiO_6 octahedra are distorted leading to a "3 + 3" coordination for titanium. But, more remarkable is the difference between the size of the $Ti1–O_6$ and $Ti2–O_6$ octahedra. One indeed observes (Table III) that the Ti2–O distances are much greater than the Ti1–O distances for the two oxides $K_{1.75}Ti_2(PO_4)_3$ and $K_2Ti_2(PO_4)_3$. This suggests that the Ti2 sites are preferentially occupied by the Ti^{III} ions, whereas the Ti^{IV} would be localized on the Ti1 sites. The fact that $KTi_2(PO_4)_3$ (*6*) exhibits only a small difference between the Ti1–O and Ti2–O distances is in agreement with this point of view and confirms that this compound contains only small amounts of Ti^{III}. In order to check the validity of this hypothesis, calculations of the mean valence of titanium in those oxides, using the Zachariasen curve (*7*), were performed. These values do not agree as well as in the molybdenum compound but the sum of the calculated valences increases when the amount of K decreases. One observes that in $KTi_2(PO_4)_3$ the calculated valences of the two titanium are almost equal and that in the two other compounds one site is occupied by Ti^{IV} and the other one by $Ti^{IV} + Ti^{III}$ for $K_{1.75}Ti_2(PO_4)_3$ and Ti^{III} for $K_2Ti_2(PO_4)_3$.

In the same way, the two potassium sites are rather different despite this same ninefold coordination. The distribution of the K^+ ions is not statistical: one site K1 is preferentially occupied whereas the second position K2 tends to be empty. Moreover the mean K1–O distance corresponding to the "fully" occupied sites is significantly greater than the mean distance K2–O (Table III), whatever the occupancy may be. Nevertheless, the two oxides $K_{1.75}Ti_2(PO_4)_3$ and $K_2Ti_2(PO_4)_3$ exhibit a different distribution of the K–O distances compared to $KTi_2(PO_4)_3$. In those two compounds the K1–O distances vary over a wide range, with very short distances (2.813–2.838 Å) and very long distances (3.145–3.188 Å), whereas the $KTi_2(PO_4)_3$ exhibits more uniform K1–O distances ranging from 2.943 to 3.076 Å. A different behavior is also observed for the K2–O distances which are quite uniform in $K_{1.75}Ti_2(PO_4)_3$ and $K_2Ti_2(PO_4)_3$ (2.895 to 2.943 Å) but show greater variation in $KTi_2(PO_4)_3$ (2.817 to 2.973 Å).

This study offers the possibility of large deviations from stoichiometry in the Langbeinite framework, which must be considered as a true cage structure, and shows the existence of mixed-valence (Ti^{III}–Ti^{IV}) involving ordering on the octahedral sites.

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