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A New Phosphate of Trivalent Titanium $Mg_3Ti_4P_6O_{24}$*

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A new Ti(III) phosphate, $Mg_3Ti_4P_6O_{24}$, has been isolated; its structure has been determined from a single-crystal X-ray diffraction study. The triclinic cell, space group $P\bar{1}$, is characterized by the following parameters: a = 6.9311(8) Å, b = 7.9616(5) Å, c = 9.4299(14) Å, α = 67.614(9)°, β = 69.348(12)°, γ = 79.327(8)°. The framework consists of (Ti, Mg)O_6 isolated octahedra, [Ti_2O_{10}] and [(Ti, Mg)$_2O_{10}$] octahedral units sharing their corners and linked via PO_4 tetrahedra. The [M_2O_{10}] units are formed of two edge-sharing MO_6 octahedra. The remaining Mg are linked to five oxygen atoms which delimit a bipyramid. The relationships between this structure and those of vanadophosphates are studied.

Inorganic phosphate materials represent a wide field of investigation which appears promising for various applications. The association of octahedral units of a transition metal with PO_4 tetrahedra allows mixed framework phosphates to be synthesized. Such compounds are interesting for their physical properties, owing to the ability of the transition metal to take various oxidation states. Titanium is a potential subject owing to its two oxidation states, III and IV. In addition to the well-known nasicon-type oxides (*1–3*) which exhibit ion exchange properties and ionic conductivity, two forms of sodium titanium (III) diphosphates, α and β $NaTiP_2O_7$ (*4*) were recently isolated. In the same way a mixed valence nonstoichiometric titanophosphate $K_{2-x}Ti_2(PO_4)_3$ (*5*) belonging to the langbeinite structure was studied. On the other hand very few titanophosphates of divalent cations are known. In a recent study a new family of titanophosphates, $ATi_2P_3O_{12}$, with the nasicon structure and characterized by a mixed valence of titanium was synthesized for A = Ca, Sr, Ba (*6*). Therefore, it appeared interesting to investigate titanophosphates of smaller divalent cations such as magnesium. We report here on the structure of a new phosphate of magnesium and trivalent titanium, $Mg_3Ti_4P_6O_{24}$.

Synthesis

The pure phase, $Mg_3Ti_4P_6O_{24}$, was synthesized in two steps. First, an adequate mixture of $MgCO_3$, $H(NH_4)_2PO_4$ and TiO_2 was heated to 673 K in air, in order to eliminate H_2O, CO_2, and NH_3. In the second

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* Dedicated to Professor Reginald Gruehn on the occasion of his 60th birthday.

0022-4596/90 $3.00

TABLE I

$Mg_3Ti_4P_6O_{24}$: INTERRETICULAR DISTANCES

$h\ k\ l$	d_{obs}	d_{calc}	I	$h\ k\ l$	d_{obs}	d_{calc}	I
0 1 0	7.369	7.349	9	0 1 4	2.201	2.202	3
0 1 1	6.773	6.772	3	$\bar{2}$ 2 1	2.158	2.161	12
1 0 1	5.786	5.767	14	0 $\bar{3}$ 1		2.157	
1 1 1	5.374	5.374	4	$\bar{2}$ 0 2	2.127	2.129	4
1 1 0	4.766	4.773	12	1 2 $\bar{2}$	2.105	2.107	4
1 1 2	4.283	4.284	27	2 $\bar{1}$ 3		2.105	
0 0 2	4.148	4.144	5	3 1 1	2.093	2.091	12
$\bar{1}$ 1 1	3.924	3.919	10	1 3 4	2.064	2.066	5
0 2 1	3.890	3.890	8	2 2 $\bar{1}$	2.049	2.051	5
0 2 0	3.674	3.674	12	1 $\bar{3}$ 1		2.047	
1 2 1	3.624	3.622	24	2 0 4	2.027	2.023	3
1 1 $\bar{1}$	3.487	3.486	6	3 2 2	2.007	2.007	11
0 2 2	3.386	3.383	15	2 3 0	1.948	1.951	10
1 2 0	3.215	3.217	18	3 1 0		1.950	
2 0 1	3.144	3.136	27	3 $\bar{1}$ 1	1.933	1.934	8
2 1 2	3.005	3.003	100	1 $\bar{2}$ 3		1.930	
0 1 3	2.941	2.939	52	$\bar{3}$ 1 0	1.895	1.893	3
1 2 3	2.855	2.857	20	0 4 0	1.838	1.837	12
2 1 0	2.825	2.842	12	0 $\bar{1}$ 4		1.836	12
$\bar{2}$ 1 0	2.709	2.711	17	2 2 5	1.819	1.822	5
2 2 1	2.648	2.649	3	3 2 4		1.818	
$\bar{1}$ 2 2	2.618	2.619	14	2 $\bar{3}$ 1	1.772	1.773	7
1 2 $\bar{1}$		2.613		$\bar{2}$ 0 3		1.772	
0 3 2	2.526	2.521	7	2 4 1	1.735	1.737	5
2 2 3	2.470	2.472	5	2 3 5		1.735	
2 1 $\bar{1}$		2.466		1 2 $\bar{3}$	1.732	1.733	9
0 3 0		2.449		0 3 5	1.661	1.663	7
2 $\bar{1}$ 2	2.445	2.449	10	2 $\bar{3}$ 2	1.643	1.643	4
2 0 3		2.440		3 $\bar{2}$ 2		1.642	
2 2 0		2.387		3 2 $\bar{1}$		1.611	
2 1 $\bar{1}$	2.383	2.382	5	1 4 $\bar{1}$	1.610	1.610	9
1 $\bar{1}$ 3		2.381		$\bar{3}$ 0 2		1.609	
1 1 4	2.347	2.347	1	1 4 5	1.601	1.602	8
0 3 3	2.256	2.257	3	$\bar{3}$ 1 2		1.601	
$\bar{1}$ 0 3		2.255		3 3 5	1.578	1.578	22

step, the resulting finely ground product was mixed with an appropriate amount of titanium and sealed in an evacuated silica ampoule. This sample was then heated to 1373 K for a week and quenched at room temperature.

Single crystals of this phase were obtained by a transport chemical method using impure $BaCl_2$ containing magnesium. Mixtures of TiO_2 and $H(H_4N)_2PO_4$ were first heated in air in order to eliminate H_2O and NH_3; then, in a second step, appropriate amounts of titanium and $Ba_{1-x}Mg_xCl_2$ were added, and the intimate mixture was heated to 1373 K in an evacuated silica ampoule for 3 days. The $Mg_3Ti_4P_6O_{24}$ composition of the crystals was determined by microprobe analysis. The X-ray diffraction powder pattern was found to be identical to that of the bulk obtained by quantitative synthesis. It was indexed (Table I) in a triclinic cell in agreement with the parameters deduced from the single-crystal study (Table II).

Structure Determination

A yellowish-purple crystal with dimensions 0.34 × 0.19 × 0.07 mm was selected for the structure determination.

The cell parameters reported in Table II were determined and refined by diffractometric techniques at 294 K with a least-squares refinement based upon 25 reflections with $18° < \theta < 22°$.

The data were collected on a CAD-4 Enraf-Nonius diffractometer with the data

TABLE II

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT PARAMETERS FOR $Mg_3Ti_4P_6O_{24}$

1. Crystal data	
Space group	$P\bar{1}$
Cell dimensions	$a = 6.3911(8)$ Å, $\alpha = 67.614(9)°$ $b = 7.9616(5)$ Å, $\beta = 69.348(12)°$ $c = 9.4299(14)$ Å, $\gamma = 79.327(8)°$
Volume	$V = 414.4$
Z	1
2. Intensity measurement	
$\lambda(MoK\alpha)$	0.71073 Å
Scan mode	$\omega - 4/3\theta$
Scan width (°)	$0.95 + 0.35 \tan \theta$
Slit aperture (mm)	$1. + \tan \theta$
Max θ (°)	45°
Standard reflections, three measured every 2000 sec (no decay)	
Reflections with $I > 3\sigma$ 5373	
3. Structure solution and refinement	
Parameters refined	169
Agreement factors	$R = 0.021$, $R_w = 0.022$
dp max.	1.02 e Å^{-3}

collection parameters reported in Table II. The reflections were corrected for Lorentz and polarization effect; no absorption corrections were performed.

Atomic coordinates of the heaviest atoms were deduced from the Patterson function and the other atoms were located by subsequent Fourier series. Initially titanium was placed on the TiMg1 position and magnesium on the TiMg2 position according to the formula $Mg_3Ti_4P_6O_{24}$ deduced from the microprobe analysis. The refinement of the atomic coordinates with isotropic thermal factors led to a high B value for TiMg1 and a negative value for TiMg2. Titanium was then distributed over TiMg1 and TiMg2 sites and the refinement led again to high B values for these two positions. Finally the occupancy factors of these two positions were refined using the titanium diffusion tables. The number of electrons obtained after refinement corresponds to a preferential occupancy of both sites by titanium (2/3 Ti; 1/3 Mg), magnesium and titanium being distributed at random over the two positions (Ti, Mg1) and (Ti, Mg2). On the other hand the third octahedral cationic site was found to be occupied only by titanium; under these conditions the R factors were lowered to $R = 0.038$ and $R_w = 0.044$ with $w = 1$. The refinement of the atomic coordinates and the anisotropic thermal factors of all the atoms of the crystal led to $R = 0.021$ and $R_w = 0.022$ for the results given in Table III[1]. Atomic scattering factors and anomalous dispersion factors were taken from international tables for X-ray crystallography (*13*).

TABLE III

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z	B(A2)
Ti	−0.02701(2)	0.22092(2)	0.47552(1)	0.440(1)
TiMg1	0.77344(2)	0.03995(2)	0.12286(2)	0.495(2)
TiMg2	0.500	0.500	0.000	0.600(3)
Mg	0.49665(5)	0.68976(4)	0.28653(4)	0.569(4)
P(1)	0.04248(3)	0.64357(2)	0.22790(2)	0.355(2)
P(2)	0.52306(3)	0.27522(3)	0.36916(2)	0.394(2)
P(3)	0.25010(3)	0.08515(2)	0.16701(2)	0.364(2)
O(1)	−0.14739(9)	0.31374(8)	0.66518(6)	0.588(7)
O(2)	−0.0020(1)	0.44417(8)	0.29391(8)	0.769(8)
O(3)	−0.3728(1)	0.28525(9)	0.49140(7)	0.781(8)
O(4)	0.2844(1)	0.2240(1)	0.46119(8)	0.884(9)
O(5)	0.0974(1)	0.04202(8)	0.34575(6)	0.565(7)
O(6)	0.46264(9)	−0.04347(8)	0.16568(7)	0.559(7)
O(7)	0.81889(9)	−0.24363(8)	0.22662(7)	0.564(7)
O(8)	0.7856(1)	0.31067(8)	−0.05597(7)	0.639(8)
O(9)	0.6636(1)	0.13884(9)	0.29106(7)	0.868(8)
O(10)	0.88489(9)	−0.03842(8)	−0.08073(6)	0.570(7)
O(11)	0.5303(1)	0.46389(8)	0.23290(7)	0.726(8)
O(12)	0.3179(1)	0.27954(9)	0.08618(8)	0.856(9)

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(\frac{4}{3}) \times [a2 \times B(1,1) + b2 \times B(2,2) + c2 \times B(3,3) + ab(\cos\gamma) \times B(1,2) + ac(\cos\beta) \times B(1,3) + bc(\cos\alpha) \times B(2,3)]$.

Description of the Structure and Discussion

Despite its formula, $Mg_{1.5}Ti_2P_3O_{12}$, close to that of nasicon or langbeinite structures, the titanophosphate $Mg_3Ti_4P_6O_{24}$ exhibits a very different and original structure. The framework $[MgTi_4P_6O_{24}]$ consists of corner and edge-sharing TiO_6 and $(Ti, Mg)O_6$ octahedra linked via PO_4 tetrahedra (Fig. 1). This host lattice delimits triangular bipyramids where magnesium cations are located. Three sorts of octahedral units can be distinguished: the $[Ti_2O_{10}]$ and $[(Ti, Mg1)_2O_{10}]$ units formed of two edge-sharing TiO_6 and or MgO_6 octahedra, respectively, and the single $(Ti, Mg_2)O_6$ octahedra. One remarkable feature of this structure deals with the fact that a great number of oxygen atoms are shared by three polyhedra simultaneously. It results in a significant distortion of the polyhedra.

The three independent PO_4 tetrahedra exhibit an almost regular "O_4" tetrahedral geometry but their P–O distances vary notably, ranging from 1.508 to 1.560 Å (Table IV). The longer P–O distances (mean value

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[1] Lists of structure factors and anisotropic thermal motion parameters are available on request to the authors.

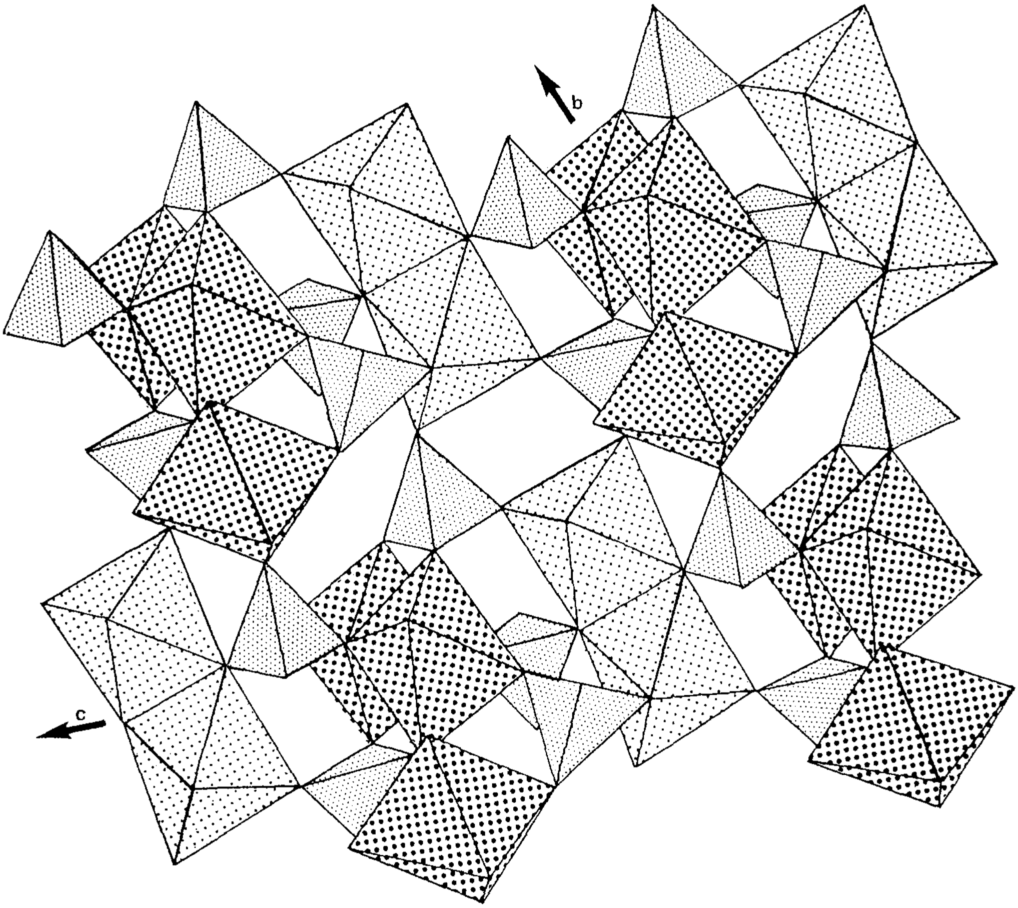

FIG. 1. Projection of the structure onto the *bc* plane.

1.55 Å) correspond to the oxygen atoms which are shared by more than two polyhedra, i.e., those common to the PO_4 tetrahedron and to two MO_6 octahedra (M = Ti or Mg) or to one MO_6 octahedron and one MgO_5 bipyramid.

The octahedra corresponding to the Ti (Ti, Mg1) and Ti, Mg2) atoms are all strongly distorted as shown from the O–O distances and O–M–O angles which spread over a wide range of values (Table V). It is worth pointing out that the M–O bonds corresponding to an oxygen atom shared by three polyhedra are significantly longer (mean distance 2.16 Å) than those involving oxygen atoms shared by two polyhedra only (mean distance 1.96 Å). The $[Ti_2O_{10}]$ units which indeed share their corners with 10 PO_4 tetrahedra (Fig. 2A) and their edges with two MgO_5 bipyramids, exhibit four triply bonded oxygen atoms and consequently present four larger Ti–O bonds per TiO_6 octahedron. In the same way the $[(TiMg1)_2O_{10}]$ units which share their corners with eight tetrahedra (Fig. 2B) and two $(TiMg_2)O_6$ octahedra and their edges with two MgO_5 bipyramids exhibit five triply bonded oxygen atoms leading to five longer M–O distances per MO_6 octahedron. The $(TiMg_2)O_6$ octahedron which shares its corners with six PO_4 tetrahedra, two $[(TiMg1)_2O_{10}]$ units, and two MgO_5 groups,

TABLE IV

DISTANCES (Å) AND ANGLES (°) IN THE PO_4 TETRAHEDRA

P(1)	O(1$^{\mathrm{iv}}$)	O(2)	O(7$^{\mathrm{vi}}$)	O(8$^{\mathrm{iii}}$)
O(1$^{\mathrm{iv}}$)	1.5505(6)	2.507(1)	2.531(1)	2.502(1)
O(2)	110.00(4)	1.5093(7)	2.480(1)	2.496(1)
O(7$^{\mathrm{vi}}$)	109.84(3)	108.72(4)	1.5418(6)	2.559(1)
O(8$^{\mathrm{iii}}$)	107.47(4)	109.22(4)	111.58(3)	1.5525(6)
P(2)	O(3$^{\mathrm{vii}}$)	O(4)	O(9)	O(11)
O(3$^{\mathrm{vii}}$)	1.5522(6)	2.462(1)	2.500(1)	2.539(1)
O(4)	107.13(4)	1.5075(7)	2.527(1)	2.519(1)
O(9)	108.92(4)	113.16(4)	1.5198(7)	2.481(1)
O(11)	109.51(4)	110.57(4)	107.50(4)	1.5566(7)
P(3)	O(5)	O(6)	O(10$^{\mathrm{viii}}$)	O(12)
O(5)	1.5602(6)	2.508(1)	2.472(1)	2.565(1)
O(6)	107.93(3)	1.5458(6)	2.514(1)	2.484(1)
O(10$^{\mathrm{viii}}$)	105.50(3)	109.04(3)	1.5458(6)	2.532(1)
O(12)	113.34(4)	108.97(4)	111.90(4)	1.5103(7)

Note. Symmetry code: (iii) $1 - x, 1 - y, -z$; (iv) $-x, 1 - y, 1 - z$; (vi) $x - 1, 1 + y, z$; (vii) $1 + x, y, z.$; (viii) $1 - x, -y, -z$.

TABLE V

DISTANCES (Å) AND ANGLES (°) IN THE $TiMgO_6$ OCTAHEDRA

TiMg1	O(6)	O(7)	O(8)	O(9)	O(10)	O(10$^{\mathrm{ii}}$)
O(6)	2.0660(6)	2.633(1)	3.347(1)	2.868(1)	2.869(1)	4.088(1)
O(7)	79.39(2)	2.1010(6)	4.209(1)	3.239(1)	2.652(1)	2.811(1)
O(8)	104.48(2)	160.92(2)	2.1671(6)	2.894(1)	2.814(1)	2.982(1)
O(9)	92.68(3)	108.21(3)	90.61(3)	1.8946(7)	3.977(1)	3.036(1)
O(10)	87.31(2)	78.53(3)	82.74(3)	173.13(3)	2.0894(6)	2.735(1)
O(10$^{\mathrm{ii}}$)	161.47(3)	84.61(2)	89.27(2)	99.65(3)	82.09(2)	2.0757(6)
TiMg2	O(8)	O(8$^{\mathrm{iii}}$)	O(11$^{\mathrm{iii}}$)	O(11)	O(12$^{\mathrm{iii}}$)	O(12)
O(8)	2.1887(6)	4.377(1)	2.972(1)	3.198(1)	2.129(1)	2.826(1)
O(8$^{\mathrm{iii}}$)	180.00	2.1887(6)	3.198(1)	2.972(1)	2.826(1)	3.129(1)
O(11$^{\mathrm{iii}}$)	85.81(2)	94.19(2)	2.1777(7)	4.355(1)	3.086(1)	2.857(1)
O(11)	94.19(2)	85.81(2)	180.00	2.1777(7)	2.857(1)	3.086(1)
O(12$^{\mathrm{iii}}$)	95.83(3)	84.17(3)	94.42(3)	85.58(3)	2.0245(7)	4.049(1)
O(12)	84.17(3)	95.83(3)	85.58(3)	94.42(3)	180.00	2.0245(7)

Note. Symmetry code: (ii) $2 - x, -y, -z$; (iii) $1 - x, 1 - y, -z$.

has four long M–O bonds corresponding to the triply bonded oxygen atoms and two shorter ones. Thus, the octahedron is also strongly distorted. The Ti–Ti distance, determined to be 3.366 Å in Ti_2O_{10} units, indicates a displacement of both atoms in opposite directions with respect to the common edge of the two octahedra, due to the high charge of the cations. On the other hand, the Ti–Mg distance of 3.141 Å in $[Ti, Mg_1]_2O_{10}$ units, considerably smaller than the previously value can be explained by the smaller charge of Mg^{2+} in this latter case.

The MgO_5 bipyramid, which shares each of its corners with one PO_4 tetrahedron and one octahedron simultaneously, exhibits distances close to those observed in the MO_6 octahedra (Table VI). This shows that this latter ion cannot be considered an interpolated cation despite its particular coordination. Consequently the structure described here can be considered near to a close packed structure. The ratio of the calculated volume of the cations and anions to the volume cell, using the ionic radii of Shannon (*7*) of 0.687, is in agreement with this point of view (*13*).

Despite its great complexity, this structure exhibits striking similarities with that of $V_2P_2O_9$ (*8*). The latter (Fig. 3) is charac-

TABLE VI

DISTANCES (Å) AND ANGLES (°) IN THE TiO_6 OCTAHEDRON AND THE MgO_5 POLYHEDRON

Ti	O(1)	O(2)	O(3)	O(4)	O(5$^{\mathrm{i}}$)	O(5)
O(1)	2.0401(6)	3.081(1)	2.623(1)	2.898(1)	2.828(1)	4.073(1)
O(2)	101.89(3)	1.9264(7)	2.625(1)	2.766(1)	4.037(1)	3.028(1)
O(3)	77.73(2)	80.24(3)	2.1386(7)	4.057(1)	3.067(1)	3.410(1)
O(4)	93.10(3)	91.03(3)	165.62(3)	1.9509(6)	3.098(1)	2.734(1)
O(5$^{\mathrm{i}}$)	85.29(2)	167.73(3)	91.75(3)	98.57(3)	2.1336(6)	2.595(1)
O(5)	160.39(3)	97.66(3)	107.36(3)	85.00(3)	75.74(3)	2.0929(6)
Mg	O(1$^{\mathrm{iv}}$)	O(3$^{\mathrm{iv}}$)	O(6$^{\mathrm{v}}$)	O(7$^{\mathrm{v}}$)	O(11)	
O(1$^{\mathrm{iv}}$)	2.1182(7)	2.623(1)	2.821(1)	4.139(1)	2.842(1)	
O(3$^{\mathrm{iv}}$)	78.31(3)	2.0350(7)	2.975(1)	3.105(1)	3.623(1)	
O(6$^{\mathrm{v}}$)	86.31(3)	94.87(3)	2.0043(7)	2.633(1)	3.694(1)	
O(7$^{\mathrm{v}}$)	166.82(3)	98.98(3)	81.04(3)	2.0488(7)	3.199(1)	
O(11)	87.19(3)	127.64(3)	134.43(3)	104.33(3)	2.0021(7)	

Note. Symmetry code: (i) $-x, -y, 1 - z$; (iv) $-x, 1 - y, 1 - z$; (v) $x, 1 + y, z$.

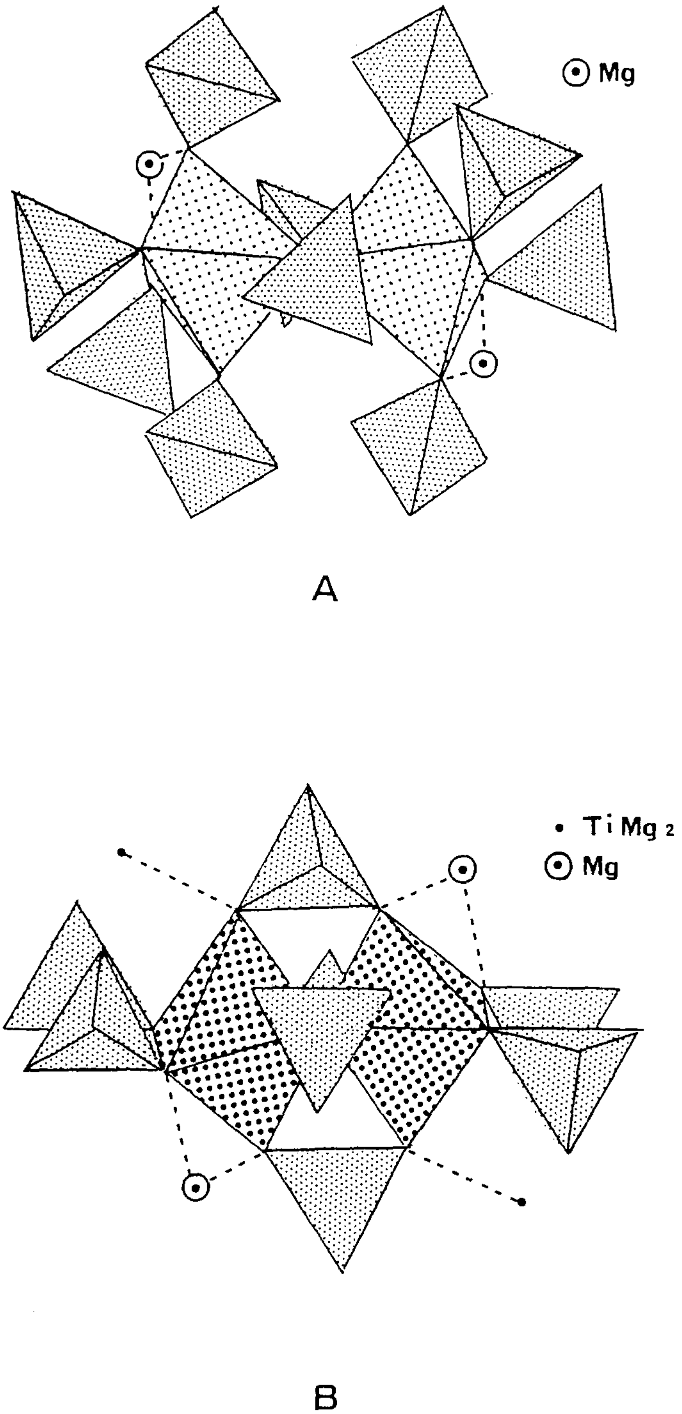

FIG. 2. (A) Neighborhood of the $[Ti_2O_{10}]$ groups. (B) Neighborhood of the $[(Ti, Mg1)_2O_{10}]$ groups; the dots represent the Mg atoms of the bipyramid.

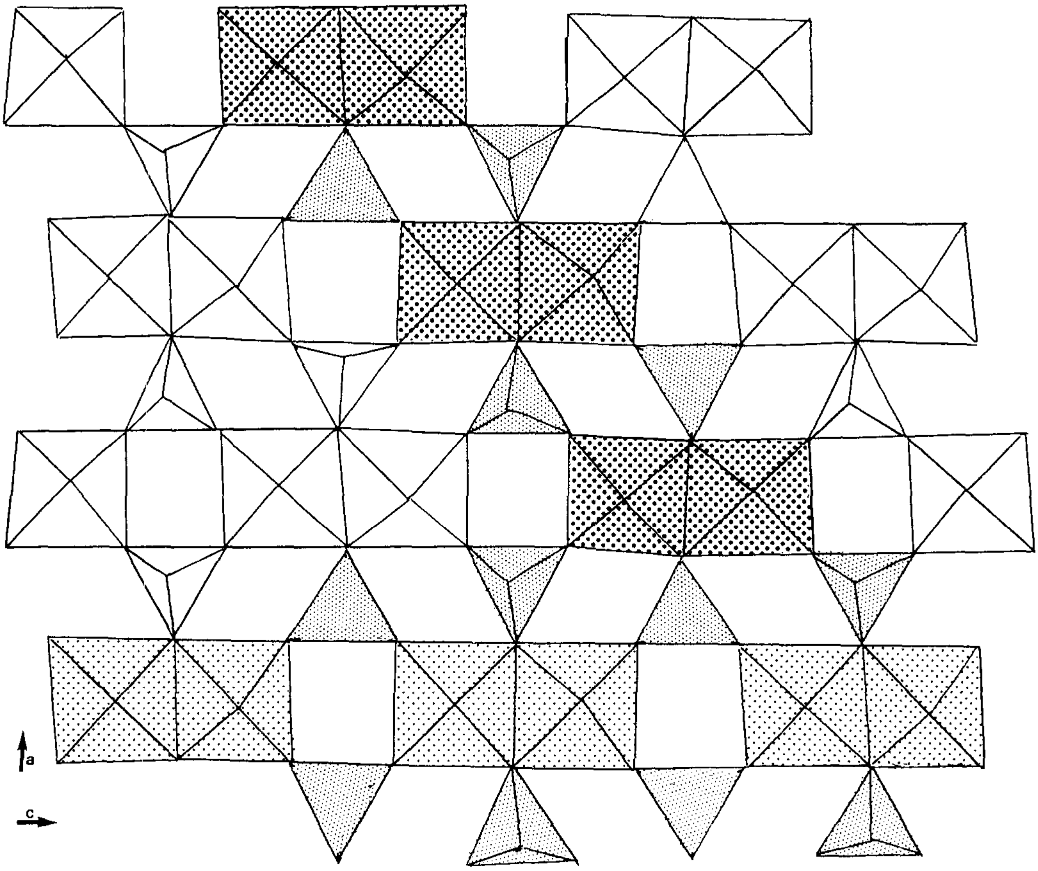

FIG. 3. Projection of the structure of $V_2P_2O_9$ onto the (010) plane. The $[V_2P_4O_{20}]$ ribbons running along [001] and [101] are differently stippled.

terized by similar $[V_2O_{10}]$ units linked via diphosphate groups. The $[Ti_2O_{10}]$ units and PO_4 tetrahedra form infinite ribbons $[Ti_2P_4O_{20}]$ running along *b* whose geometry is very similar to the ribbon $[V_2P_4O_{20}]$ (Fig. 3) running along [001] in the VP_2O_9 cell, except that diphosphate groups replace single PO_4 tetrahedra in the phosphate of vanadium. In the same way, the $[(Ti, Mg1)_2O_{10}]$ units and PO_4 tetrahedra form infinite $[(Ti, Mg1)_2P_4O_{20}]$ ribbons running along *a* (Fig. 4B) which can be compared to the $[V_2P_4O_{20}]$ ribbons drawn by considering the structure of $V_2P_2O_9$ along the [101] direction of the cell (Fig. 3).

Another interesting feature of this structure deals with its relationships with several other phosphates such as $MoPO_5$ (*9*), Na $MoPO_6$ (*10*), $KNb_3P_3O_{15}$ (*11*), or $K_7Nb_{14}P_9O_{60}$ (*12*). Like all those phosphates, it indeed exhibits infinite chains $[TiPO_8]$ and $[(Ti, Mg)_1PO_8]$ running along *a* (Fig. 4A and 4B), in which one octahedron alternates with one tetrahedron. Such chains share the edges of their octahedra in two different ways forming double chains $[Ti_2P_2O_{14}]$ or $[(Ti, Mg1)_2P_2O_{14}]$.

It is worth pointing out that no unidimensional conductivity should be expected in this phase despite the existence of infinite chains of edge and corner-sharing octahedra running along the direction [110] (Fig.

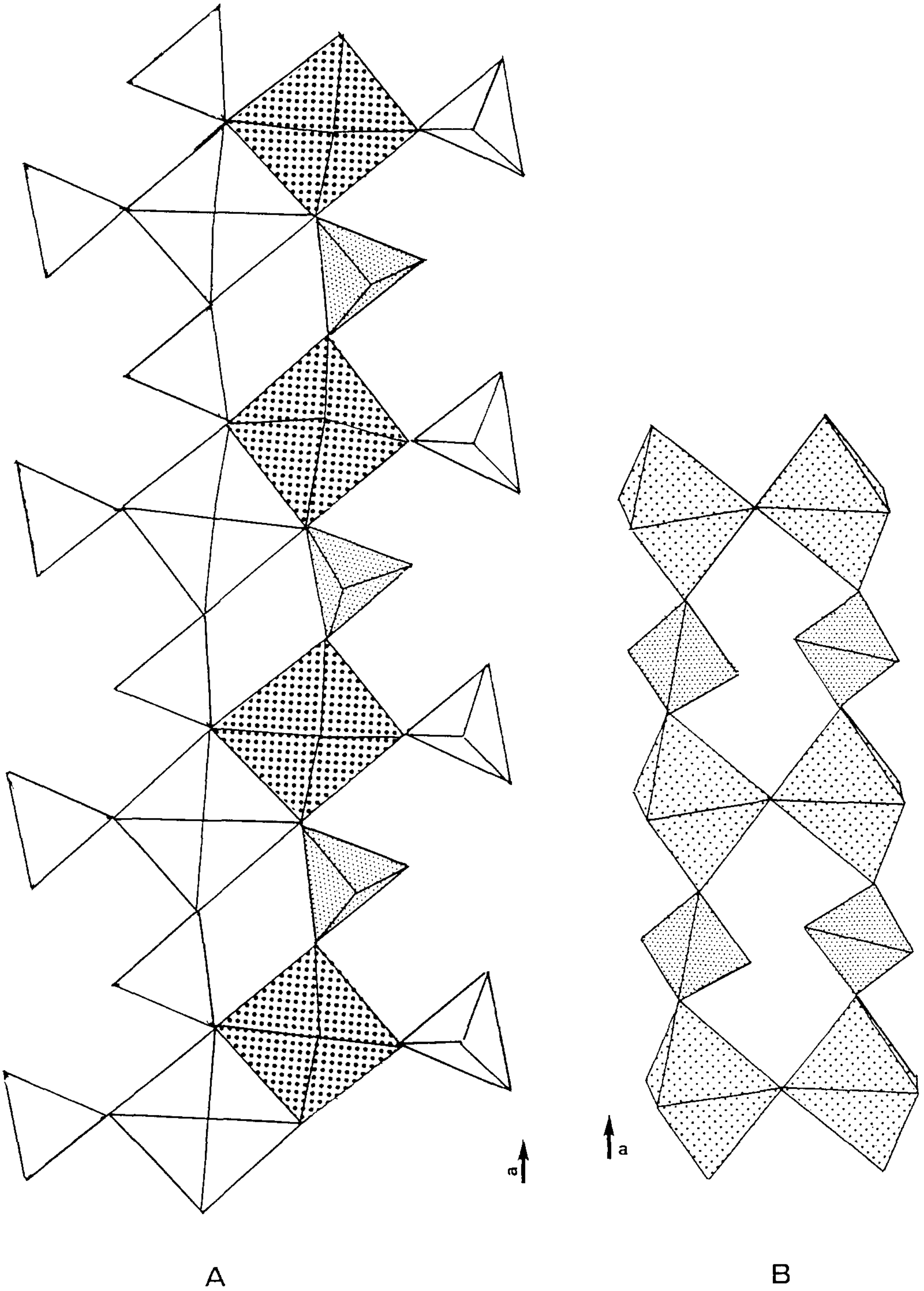

FIG. 4. (A) Infinite $TiPO_5$ chains (stippled) running along *a* sharing the edges of their octahedra. (B) infinite $[(TiMg1)_2P_4O_{20}]$ ribbons and infinite $[(TiMg1)PO_5]$ chains (stippled) running along *a*.

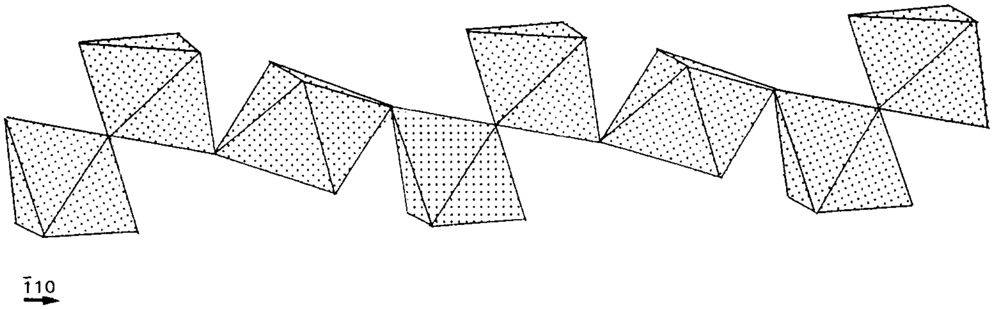

FIG. 5. Infinite chains of $(\mathrm{Ti, Mg})\mathrm{O}_6$ running along [110].

5), and of the d^1 character of titanium (III). Such chains are indeed built up from $[(\mathrm{Ti, Mg1})_2\mathrm{O10}]$ units linked via $(\mathrm{Ti, Mg2})_1\mathrm{O}_6$ octahedra so that the high magnesium content prevents the overlapping of the *d* orbitals of titanium and the *p* orbital of oxygen, all over the chain. Finally the existence of $[\mathrm{Ti}_2\mathrm{O}_{10}]$ units completely isolated from the other octahedra by PO_4 tetrahedra can be considered clusters which will be studied for their magnetic properties.

References

1. H. Y. P. HONG, *Mater. Res. Bull.* **11,** 173 (1976).
2. M. BARJ, H. PERTUIS, AND PH. COLOMBAN, *Solid State Ionics* **11,** 157 (1983).
3. A. NADIRI, Thesis, Bordeaux (1986).
4. A. LECLAIRE, A. BENMOUSSA, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *J. Solid State Chem.* **77,** 299 (1988).
5. A. LECLAIRE, A. BENMOUSSA, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *J. Solid State Chem.* **78,** 227 (1989).
6. A. BENMOUSSA, M. M. BOREL, A. GRANDIN, A. LECLAIRE, AND B. RAVEAU, *Ann. Chim.* **14,** 181 (1989).
7. R. D. SHANNON, *Acta Crystallogr. A* **32,** 751 (1976).
8. YA GORBUNOVA, AND S. A. LINDE, *Dokl. Akad. Nauk SSSR* **245,** 589 (1979).
9. P. KIERKEGAARD, AND J. M. LONGO, *Acta Chem. Scand.* **24,** 427 (1970).
10. P. KIERKEGAARD, *Ark. Kemi* **18,** 553 (1962).
11. A. LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *J. Solid State Chem.* **80,** 12 (1989).
12. A. LECLAIRE, A. BENABBAS, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *J. Solid State Chem.* **82,** (1989).
13. "International Tables for X-Ray Crystallography, Kynoch Press, Birmingham (1974). (Present distributor: Kluwer Academic Publishers, Dordrecht.)