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MoP_3SiO_{11}: A Silicophosphate of Molybdenum(III)

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A new molybdenum(III) silicophosphate MoP_3SiO_{11} was synthesized. Its structure was determined from a single-crystal study in the space group $C2/c$ and the parameters $a = 14.584(2)$ Å, $b = 8.416(1)$ Å, $c = 14.180(1)$ Å, $\beta = 110.05(6)°$. The three-dimensional framework of this oxide is built of corner-sharing P_2O_7 and Si_2O_7 groups and MoO_6 octahedra. The structure of this oxide is closely related to that of $AMo_3P_6Si_2O_{25}$ (A = K, Rb, Tl); both contain identical $[Mo_2P_6Si_2O_{22}]_\infty$ slabs, in which one can recognize the $P_6Si_2O_{25}$ units. The main difference between the two structures lies in the connection of those slabs: in MoP_3SiO_{11} they are connected directly through the corners of their PO_4 tetrahedra, whereas in $AMo_3P_6Si_2O_{25}$ additional planes of octahedra are introduced between the slabs. The structural relationships between MoP_3SiO_{11} and the vanadosilicophosphate $V_3P_5SiO_{19}$ are also discussed.

Introduction

The study of oxides characterized by a mixed framework built of octahedra and tetrahedra is attractive owing to the possibility of synthesizing host lattices intermediate between those of zeolites and of octahedral bronzes with a tunnel structure. The synthesis and studies of the large family of phosphate tungsten bronzes in which PO_4 tetrahedra and P_2O_7 groups adapt the ReO_3-type framework confirm this point of view (*1*, *2*). A recent study of the molybdophosphates and molybdosilicophosphates shows that molybdenum is also a potential candidate for the formation of such structures; the chemistry of this element appears, like that of tungsten, rather rich, owing to its ability to take several oxidation states. However, contrary to tungsten, electrons could not be delocalized in the framework but would be localized on the molybdenum ions in octahedral configurations, as observed in the phosphates $K_4Mo_8P_{12}O_{52}$ (*3*), characterized by the presence of Mo(V) ions off center in the MoO_6 octahedra, and $AMo_2P_3O_{12}$ (A = K, Rb, Tl) (*4*), in which the Mo(IV) ions exhibit an octahedral coordination. A recent study of the silicophosphates $AM_3P_6Si_2O_{25}$ (*5–7*) has led us to consider for the pure molybdenum oxides two possibilities corresponding either to the presence of Mo(IV) only, characterized by the formula $AMo_3^{IV}P_{5.8}Si_2O_{25}$, or to the presence of Mo(IV) and Mo(III) simultaneously, according to the formula $AMo_2^{IV}Mo^{III}P_6Si_2O_{25}$. The present work deals with the structural study of a new silicophosphate, Mo(III) $Mo^{III}P_3SiO_{11}$, whose structure is closely related to that of $AM_3P_6Si_2O_{25}$.

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Experimental

Synthesis. The silicophosphate MoP_3SiO_{11} was prepared in two steps. First, MoO_3, SiO_2, and ammonium phosphate $(NH_4)_2HPO_4$ were mixed in an agate mortar in the molar ratios $SiO_2 : (NH_4)_2HPO_4 : MO_3 = 1:3:0.5$ and heated at 620°C to obtain the stoichiometry "$M_{0.5}P_3SiO_{11}$." The resulting mixture was than added to the required amount of molybdenum (i.e., 0.5 Mo) and heated in an evacuated silica ampoule for 12 hr at 1000°C. Single crystals could be isolated at the surface of the sintered sample.

During the investigation of the Ba–Si–P–O system, single crystals with the same composition and parameters were also isolated.

Structural determination. A yellow flat plate of 0.19 × 0.17 × 0.02 mm was selected for the structural determination.

The Laue patterns showed monoclinic symmetry (*m*). The cell parameters in "abstract" were determined by diffractometric techniques with a least-squares refinement based on 25 reflections. Systematic absences in all the space for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$ led to the space groups *Cc* or *C2/c*.

The data were collected on a CAD 4 Enraf-Nonius diffractometer using graphite-monochromatized $MoK\alpha$ radiation. The intensities were measured up to $\theta = 45°$ with an ω–θ scan of $(0.90 + 0.35 \tan \theta)°$ and a counter slit aperture of $(1.00 + \tan \theta)$ 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 intensity measured on the 600, 020, and $60\bar{2}$ reflections verified the stability of the sample. The 3287 independent reflections for which $I \geq 3\sigma(I)$ were corrected for Lorentz and polarization effects.

The Mo atomic coordinates were deduced from a three-dimensional Patterson map. The remaining atoms were located in subsequent Fourier syntheses. Scattering factors and anomalous-dispersion corrections for the different atoms of the compound were taken from the "International Tables for X-Ray Crystallography" (*8*).

TABLE I

MoP_3SiO_{11}: ATOMIC COORDINATES

Atom	x	y	z	B_{eq}
Mo	0.09088(1)	0.25000(3)	0.02267(1)	0.39(1)
P(1)	−0.03788(4)	0.04756(7)	0.14195(5)	0.47(1)
P(2)	0.31616(4)	0.09844(7)	0.14196(4)	0.49(1)
P(3)	0.38628(4)	0.10398(7)	0.35802(4)	0.47(1)
Si	0.21046(4)	0.2500712)	0.38147(4)	0.47(1)
O(1)	0.23377(14)	0.21326(25)	0.11828(16)	0.87(3)
O(2)	0.08549(15)	0.43527(24)	0.11821(16)	0.85(4)
O(3)	0.04877(14)	0.10172(26)	0.11823(16)	0.85(4)
O(4)	0.12876(16)	0.41264(27)	−0.07075(16)	0.90(4)
O(5)	0.10645(15)	0.06507(26)	−0.07045(16)	0.89(4)
O(6)	−0.05580(13)	0.27268(23)	−0.07059(15)	0.86(4)
O(7)	−0.09733(13)	0.19396(24)	0.15953(15)	0.79(3)
O(8)	0.	−0.03410(31)	0.25	0.68(5)
O(9)	0.25	0.25	0.5	1.13(5)
O(10)	0.21861(14)	0.42708(21)	0.34057(15)	0.74(3)
O(11)	0.27458(13)	0.12886(23)	0.34066(15)	0.73(3)
O(12)	0.39187(13)	0.14213(24)	0.25005(14)	0.70(3)

The atomic parameters with anisotropic thermal factors were refined by full-matrix least squares, and a linear weighting scheme $w = f[(\sin \theta)/\lambda]$ was adjusted by using the program POND (*9*). The reliability factors were lowered to $R = 0.027$ and $R_w = 0.030$ with $s = 1.33$. Final atomic parameters are given in Table I.[1]

Description of the Structure and Discussion

The structure of MoP_3SiO_{11} is built of corner-sharing MoO_6 octahedra, diphosphate groups P_2O_7, and disilicate groups Si_2O_7 (Fig. 1). Each MoO_6 octahedron shares its six corners with P_2O_7 groups, whereas in a similar way, each Si_2O_7 group is linked to six P_2O_7 groups, with the result that each P_2O_7 group shares four corners with the MoO_6

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

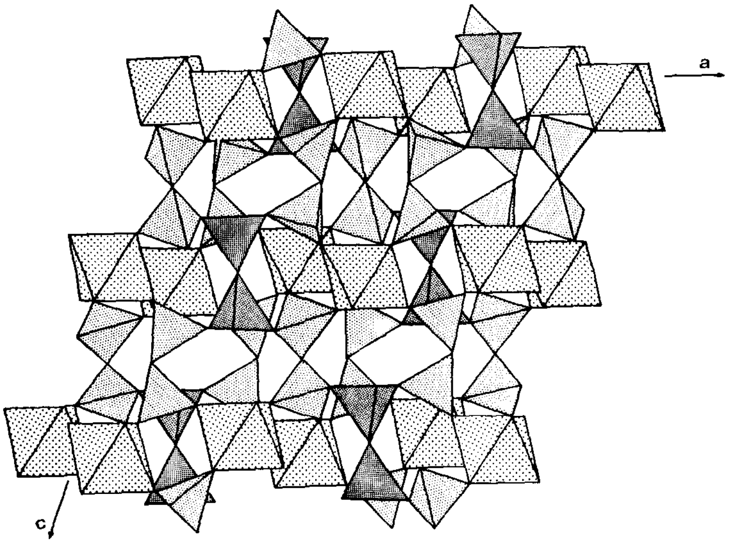

FIG. 1. Projection along **b** of the MoP_3SiO_{11} structure.

octahedra and two corners with the Si_2O_7 groups.

For each PO_4 tetrahedron, three sorts of P–O distances can be distinguished (Table IIB):

(i) the short bonds ($\langle P{-}O\rangle_6$ = 1.49 Å)[2], which corresponds to the oxygen atom common to a PO_4 tetrahedron and a MoO_6 octahedron.

(ii) the intermediate bonds ($\langle P{-}O\rangle_3$ = 1.576 Å), in which the oxygen atom is linked to a phosphorus atom and a silicon atom simultaneously.

(iii) the long bonds ($\langle P{-}O\rangle_3$ = 1.595 Å), in which the bridging oxygen atom is shared by two PO_4 tetrahedra.

Nevertheless the PO_4 tetrahedra are almost regular and the phosphorus atom is off center by about 0.11 Å with respect to the center of gravity of the "O_4" tetrahedron.

The SiO_4 tetrahedron are also quasi-regular (Table IIC): a short Si–O bond (1.579 Å) is observed for the bridging oxygen atom common to two Si whereas the three other Si–O bonds in which each oxygen atom is common to a SiO_4 and a PO_4 tetrahedron are longer ($\langle Si{-}O\rangle_3$ = 1.619 Å).

The tervalent state observed for molyb-

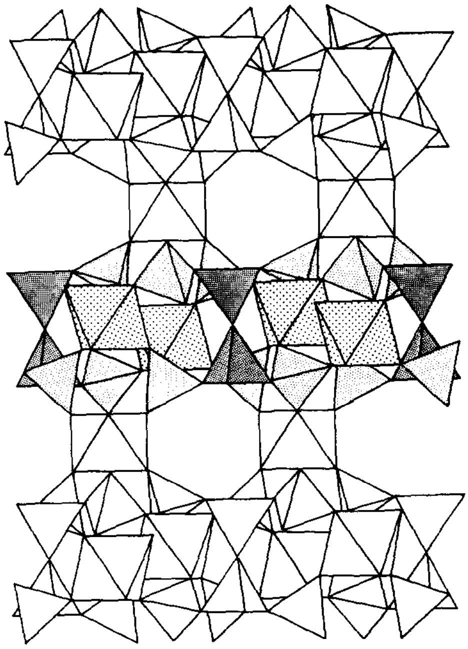

FIG. 2. Projection along **a** of the $AMo_3P_6Si_2O_{25}$ structure.

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[2] $\langle P{-}O\rangle_n$ is the mean value of n P–O bonds.

TABLE II

A. Geometry of MoO_6 Octahedron

Mo	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	2.083(2)	2.858(3)	2.856(3)	3.087(3)	2.959(3)	4.814(3)
O(2)	86.58(8)°	2.085(2)	2.858(3)	2.962(4)	4.184(3)	3.083(3)
O(3)	86.56(8)°	86.56(9)°	2.083(2)	4.187(3)	3.083(4)	2.961(3)
O(4)	94.95(9)°	89.95(9)°	176.12(9)°	2.106(3)	2.943(3)	2.939(3)
O(5)	89.98(8)°	176.19(8)°	94.85(9)°	88.74(9)°	2.103(2)	2.941(3)
O(6)	176.22(8)	94.81(8)°	90.01(8)°	88.57(8)°	88.73(8)°	2.103(2)

B. Distances and Angles in PO_4 Tetrahedra

P(1)	O(3)	O(5^{i})	O(7)	O(8)
O(3)	1.486(2)	2.550(3)	2.518(3)	2.493(3)
O(5^{i})^{a}	117.7(1)°	1.494(2)	2.500(3)	2.500(2)
O(7)	110.7(1)°	109.1(1)	1.575(2)	2.469(3)
O(8)	107.9(1)°	108.0(1)	102.3(1)	1.595(1)

P(2)	O(1)	O(4^{ii})	O(10^{iii})	O(12)
O(1)	1.488(2)	2.554(4)	2.519(3)	2.492(2)
O(4^{ii})	117.9(1)°	1.493(3)	2.499(3)	2.498(3)
O(10^{iii})	110.6(1)°	109.0(1)	1.576(2)	2.470(3)
O(12)	107.9(1)°	108.0(1)°	102.4(1)°	1.595(2)

P(3)	O(2^{iii})	O(6^{iv})	O(11)	O(12)
O(2^{iii})	1.485(2)	2.546(3)	2.519(3)	2.491(3)
O(6^{iv})	117.6(1)°	1.493(2)	2.501(3)	2.497(3)
O(11)	110.7(1)°	109.1(1)°	1.576(2)	2.469(3)
O(12)	108.0(1)°	107.9(1)°	102.3(1)°	1.594(2)

C. Distances and Angles in SiO_4 Tetrahedron

Si	O(7^{v})	O(9)	O(10)	O(11)
O(7)	1.620(2)	2.616(2)	2.641(3)	2.642(3)
O(9)	109.7(1)°	1.579(1)	2.614(2)	2.613(2)
O(10)	109.3(1)°	109.7(1)°	1.618(2)	2.639(3)
O(11)	109.3(1)°	109.6(1)°	109.2(1)°	1.619(2)

[a] Symmetry code: i, $-x, -y, -z$; ii, $\frac{1}{2} - x, \frac{1}{2} - y, -z$; iii, $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; iv, $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; v, $-x, y, \frac{1}{2} - z$.

denum in this compound must be pointed out, owing to the fact that this oxidation state is rarely observed for molybdenum in oxides. The existence of this Mo(III) silicophosphate suggests that the formula proposed for the oxide $AMo_3^{IV}P_{5.8}Si_2O_{25}$ (5–7) could be, in fact, $AMo_3P_6Si_2O_{25}$; the latter mixed valence oxide, which is also characterized by isolated MoO_6 octahedra, would present two localized states for molybdenum, corresponding to the presence of $(Mo^{IV}O_6)$ and $Mo^{III}O_6$ octahedra simultaneously in the structure. The interatomic distances Mo^{III}–O observed in MoP_3SiO_{11}

(Table IIA) are in agreement with those observed for one type of MoO_6 octahedron in $AMo_2^{IV}Mo^{III}P_6Si_2O_{25}$ (*5–7*); these octahedra are characterized by three short Mo–O distances—2.084 Å in MoP_3SiO_{11} and 2.044 Å in $RbMo_3P_6Si_2O_{25}$—and three longer Mo–O distances—2.104 Å in MoP_3SiO_{11} and 2.059 Å in $AMo_3P_6Si_2O_{25}$.

The structure of this oxide is closely related to that of $AMo_3P_6Si_2O_{25}$, as shown by a comparison of the projections along *b* (Fig. 1) and *a* (Fig. 2), respectively. Both frameworks are formed of identical mixed slabs $|Mo_2P_6Si_2O_{22}|_\infty$ built of corner-sharing Si_2O_7 groups, MoO_6 octahedra, and PO_4 tetrahedra. The projection of such a slab along [103] on the (001) plane (Fig. 3a) shows that it can be described as built of $Si_2P_6O_{25}$ units previously observed in $AMo_3P_6Si_2O_{25}$ (Fig. 3b) (*5–7*) and in the oxides $V_3P_5SiO_{19}$ (*10*)

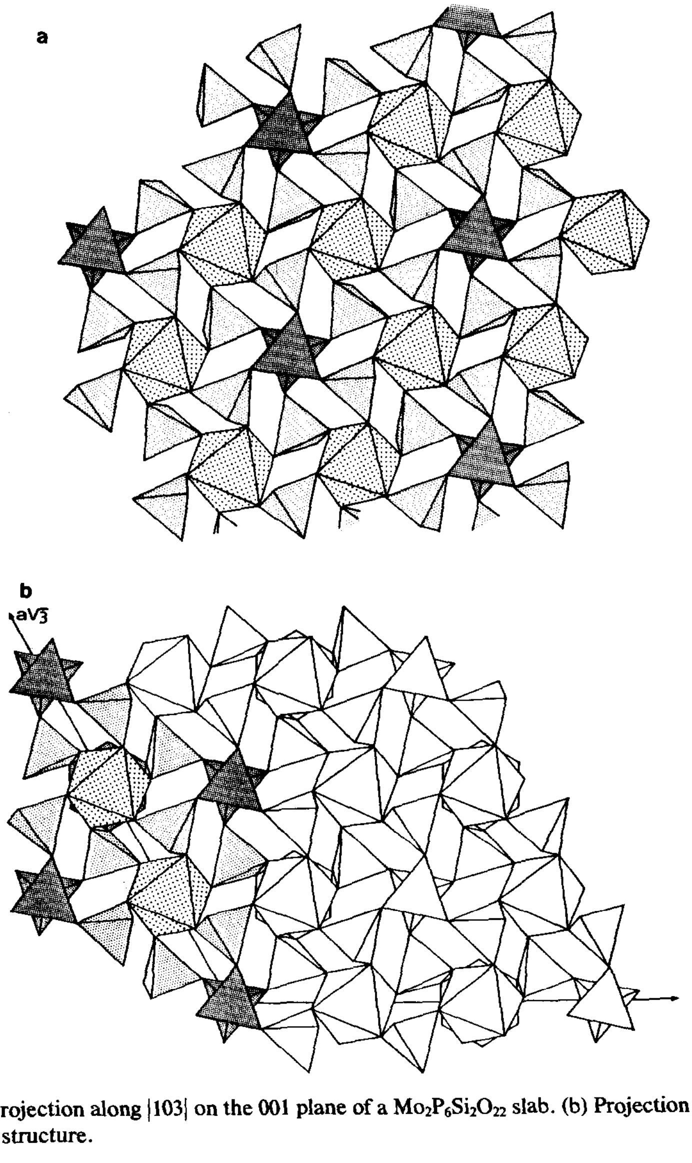

FIG. 3. (a) Projection along |103| on the 001 plane of a $Mo_2P_6Si_2O_{22}$ slab. (b) Projection along c of the $AMo_3P_6Si_2O_{25}$ structure.

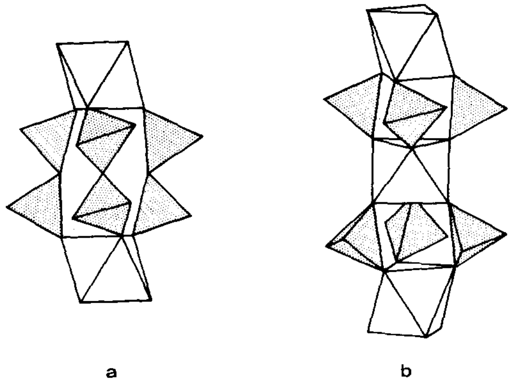

FIG. 4. Columns formed by the connection between two $Mo_2P_6Si_2O_{22}$ slabs (a) in MoP_3SiO_{11}, (b) in $AMo_3P_6Si_2O_{25}$.

and the oxide $Si_5P_6O_{25}$ (*11*). Nevertheless, these tetrahedral units of $Si_2P_6O_{25}$, unlike those of the other oxides, are not isolated in MoP_3SiO_{11}; they share the corners of the PO_4 tetrahedra, forming P_2O_7 groups which are common to two adjacent $[Mo_2P_6Si_2O_{22}]$ slabs. Consequently the P_2O_7 groups and the Si_2O_7 groups form a three-dimensional framework $[P_6Si_2O_{22}]_\infty$ which delimits octahedral cavities where the Mo(III) ions are located.

The main difference between MoP_3SiO_{11} and $AMo_3P_6Si_2O_{25}$ lies in the junction between the $[Mo_2P_6Si_2O_{22}]$ slabs along the *c* direction. In MoP_3SiO_{11} two adjacent slabs are linked directly to each other, in such a way that three PO_4 tetrahedra of one slab share their corners with the three other PO_4 tetrahedra of the second slab (Fig. 1), forming units of two octahedra connected through three P_2O_7 groups characterized by an eclipsed configuration (Fig. 4a). In $AMo_3P_6Si_2O_{25}$, two successive $[Mo_2P_6Si_2O_{22}]$ slabs are connected to each other through a "plane" of "MoO_6" octahedra whose ternary axis is parallel to *c* (Fig. 2); these additional octahedra share their vertices with the PO_4 tetrahedra, forming unit built of three octahedra and six PO_4 tetrahedra (Fig. 4b) previously described (*5*). Thus, it appears that the structure of the oxides $AMo_3P_6Si_2O_{25}$ can be deduced from that of MoP_3SiO_{11} by the simple introduction of planes of MoO_6 octahedra between the $|Mo_2P_6Si_2O_{22}|$ layers, forming intersecting tunnels where the additional *A* ions (K, Rb, Tl) are located. Consequently, a new series of oxides can be predicted to correspond to the general formulation $AMoO_3\ (Mo_2P_6Si_2O_{22})_n$, where *n* is an integral number; in this series MoP_3SiO_{11} and $AMo_3P_6Si_2O_{25}$ correspond to the members $n = \infty$ and $n = 1$, respectively. This phenomenon, the formation of additional tunnels, is closely related to the one observed in pure octahedral frameworks. It is indeed observed in the pyrochlore structure AM_2O_6 (Fig. 5a), which can be deduced from the hexagonal tungsten bronze structure AM_3O_9 (HTB slabs) by introduction of similar MO_3 planes of octahedra (12) so that it can be described as the first members of the series $AMO_3\ (AM_3O_9)_n$. Also closely related to those structures are the oxides $AMoO_3\ (AM_6O_{15})_n$ and $(AM_3O_9)_{n'}$ (*13–15*).

The structure of the vanadosilicophosphate $V_3P_5SiO_{19}$ (*10*) is also closely related to the structures of MoP_3SiO_{11} and $AMo_3P_6Si_2O_{25}$. The latter oxide is also characterized by $Si_2P_6O_{25}$ units, which are isolated as in $AMo_3P_6Si_2O_{25}$ (*5–7*). Again one observes similar mixed slabs parallel to the (001) plane of the hexagonal cell (Fig. 6a). However, in that oxide the slabs are silicon defi-

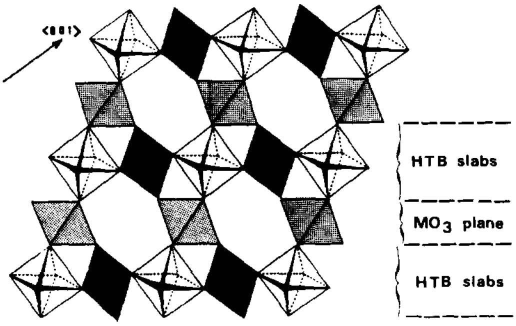

FIG. 5. Pyrochlore structure AM_2O_6.

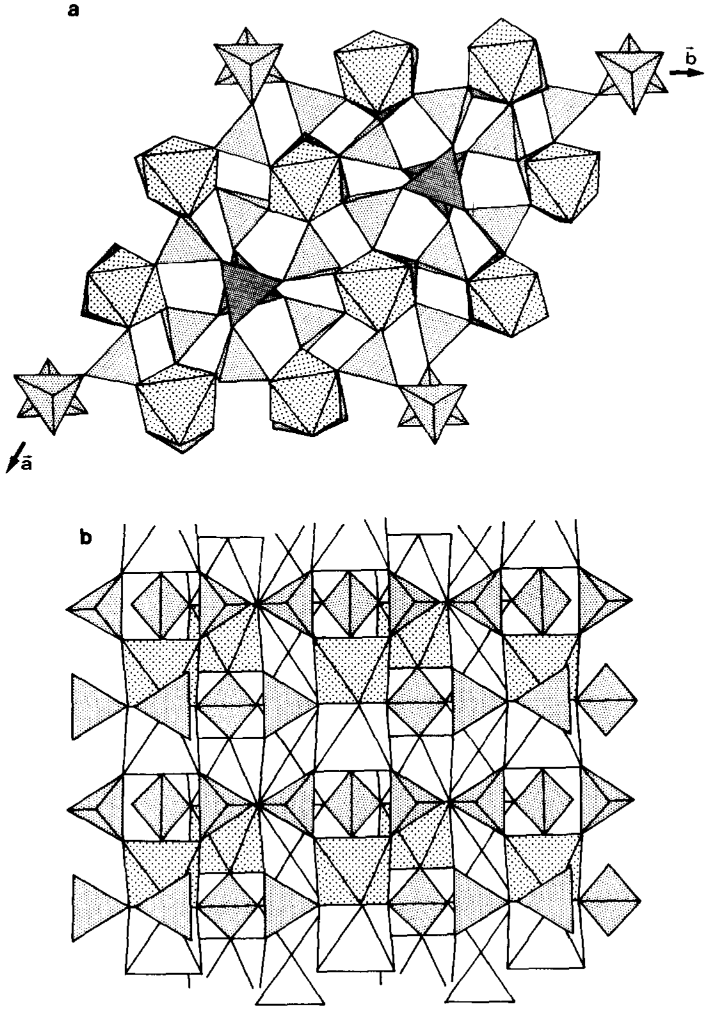

FIG. 6. Projections of $V_3P_5SiO_{19}$ structure (a) along **c**, (b) along |120| showing the connection between two $Mo_2P_6Si_2O_{22}$ slabs (shaded polyhedra) by a plane of VO_6 octahedra.

cient, so that in the same slab one row of Si_2O_7 groups alternates with two rows of SiO_4 tetrahedra. In $V_3P_5SiO_{19}$ the different slabs are connected to each other through additional VO_6 octahedra whose ternary axes are parallel to *c* (Fig. 6b) as in MoP_3SiO_{11}. However, the mode of connection is very different from that observed for MoP_3SiO_{11}; each additional VO_6 octahedron shares one face with the octahedron belonging to one slab and shares its three other vertices with the PO_4 tetrahedra belonging to the other slab, so that V_2O_9 clusters are formed.

Conclusions

The structural study of MoP_3SiO_{11} shows that the tervalent state of molybdenum is quite stable in oxides that are unambiguous. This study leads us to suggest that the formula of the intersecting tunnel structure $AMo_3P_{5.8}Si_2O_{25}$ is in fact $AMo_3P_6Si_2O_{25}$, characterized by the simultaneous presence of Mo(III) and Mo(IV) ions in octahedral coordination. The close relationships between MoP_3SiO_{11} and the oxides $AMo_3P_6Si_2O_{25}$ and $V_3P_5SiO_{11}$ show the great flexibility of the $P_6Si_2O_{25}$ units and offer a wide field of research for the synthesis of structures characterized by a mixed framework. The introduction of "planes of octahedra" similar to the phenomenon observed in octahedra frameworks such as those related to the HTBs and pyrochlore should make it possible to generate new oxides with a tunnel structure.

References

1. B. Raveau, *in* "Proceedings, Indian National Science Academi, New Delhi, **52,** 67 (1986).
2. B. Raveau, *in* "Proceedings, Indian Academy of Sciences, Bangalore, **96,** 419 (1986).
3. A. Leclaire, J. C. Monier, and B. Raveau, *J. Solid State Chem.* **48,** 147 (1983).
4. A. Leclaire, J. C. Monier, and B. Raveau, *J. Solid State Chem.* **59,** 301 (1985).
5. A. Leclaire, J. C. Monier, and B. Raveau, *Acta Crystallogr. Sect. B* **40,** 180 (1984).
6. A. Leclaire, M. M. Borel, A. Grandin, and B. Raveau, *Mater. Chem. Phys.* **12,** 537 (1985).
7. A. Leclaire, J. C. Monier, and B. Raveau, *Acta Crystallogr. Sect. C* **41,** 1719 (1985).
8. "International Tables for X-ray Crystallography," Vol. IV, p. 72, Kynoch Press, Birmingham, 1974.
9. A. Leclaire, unpublished.
10. A. Leclaire, H. Chahboun, D. Groult, and B. Raveau, *J. Solid State Chem.* **65,** 168 (1986).
11. H. Mayer, *Mon. Chem.* **105,** 46 (1974).
12. B. Raveau, *Rev. Inorg. Chem.* **1,** 81 (1979).
13. C. Michel, A. Guyomarc'h, and B. Raveau, *J. Solid State Chem.* **25,** 251 (1978).
14. C. Michel, A. Guyomarc'h, and B. Raveau, *J. Solid State Chem.* **22,** 393 (1977).
15. G. Desgardin, C. Robert, D. Groult, and B. Raveau, *J. Solid State Chem.* **22,** 101 (1977).