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$MoAlP_2O_9$ molybdenum(V) aluminophosphate isostructural with $VSiP_2O_9$

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Abstract. A new molybdenum aluminophosphate $MoAlP_2O_9$ has been isolated and its structure determined from X-Ray single crystal study. This tetragonal phase (a = 8.803 Å, c = 8.697 Å), space group *P4/ncc* is isostructural with $VSiP_2O_9$. Its structure can be described in a very simple way by the assemblage of ReO_3-type rows $[MoO_3]_\infty$ with $[AlP_2O_6]_\infty$ tetrahedral columns. The MoO_6 octahedron exhibits one very short Mo–O distance (1.654 Å) characteristic of Mo(V), to be compared with other molybdenyl phosphates and silicophosphates.

Introduction

Pentavalent molybdenum is characterized by a particular behaviour with respect to other ions with an electronic d^1 configuration such as Ti(III) or W(V). Mo(V) tends to take indeed an octahedral coordination in which one Mo(V)-O distance is very small with respect to the five other ones (~1.6 Å), so that the MoO group is often called the molybdenyl group. Nevertheless the stabilisation of Mo(V) in oxides is not currently observed; it necessitates the presence of a rather covalent matrix in which the MoO_6 octahedra can be isolated one from the other. This is the case in several phosphates and silicophosphates such as $MoPO_5$ (Kierkegaard and Westerlund, 1964), $K_4Mo_8P_{12}O_{52}$ (Leclaire, Monier and Raveau, 1983), various forms of the phases $KMo_2P_3O_{13}$ (Lii and Haushalter, 1987; Leclaire et al., 1989), $CsMo_2P_3O_{13}$ (Lii and Haushalter, 1987; Chen et al., 1988), and $AgMo_5P_8O_{33}$ (Lii, Johnston, Goshorn and Haushalter, 1987). In this respect Mo(V) exhibits some similarities with vanadium for which the vanadyl group

Table 1. Summary of crystal data, intensity measurements, and structure refinement parameters for $MoAlP_2O_9$.

1. Crystal data	
Space group	$P4/ncc$
Cell dimensions	$a = 8.8030(8)$ Å $b = 8.8030(8)$ $c = 8.6970(6)$
Volume	$V = 674.0(2)$ Å^3
Z	4
Molecular weight	328.86
Dx	3.24
2. Intensity measurement	
λ (Mo$K\alpha$)	0.71073 Å
Scan mode	$\omega - 4/3\ \theta$
Scan width (°)	$1.00 + 0.35 \tan\theta$
Slit aperture (mm)	$1.00 + \tan\theta$
max θ (°)	45
Standard reflections	3 measured every 2000 s (no decay)
Reflections with $I > 2.5\ \sigma$	578
μ (mm^{-1})	2.52
3. Structure solution and refinement	
Parameters refined	32
Agreement factors	$R = 0.027$, $R_w = 0.031$

is stabilized in several vanadium phosphates such as α- and β-VPO_5 (Gopal et al., 1972; Jordan et al., 1973), $V_2P_2O_9$ (Gorbunova et al., 1979) and in the silicophosphate $VSiP_2O_9$ (Middelmiss et al., 1976). Among the different elements susceptible to participate in a tetrahedral matrix aluminium is a good candidate. For this reason the system Mo–Al–P–O was investigated. We report here on the structure of a new molybdenum(V) aluminophosphate $MoAlP_2O_9$.

Sample preparation and crystal growth

The molybdenum(V) aluminophosphate $MoAlP_2O_9$ was prepared in the form of powder in two steps. In the first step, a mixture of $H(NH_4)_2PO_4$, Al_2O_3 and MoO_3, was heated up to 673 K in air, in order to eliminate H_2O, CO_2 and NH_3. In a second step, the resulting finely ground powder was mixed with the appropriate amount of molybdenum and sealed in an evacuated silica ampoule. This sample was heated up to 1273 K for 18 hours and quenched at room temperature.

Single crystals of this phase were obtained in the preparation of the phase $KMo_3P_8O_{28}$. This preparation was performed in two steps. $H(NH_4)_2PO_4$, K_2CO_3 and MoO_3, were heated up to 673 K in air, in order to eliminate H_2O, CO_2 and NH_3. In a second step, the resulting powder was mixed with the appropriate amount of molybdenum; this sample put in an alumina tube was sealed in an evacuated silica ampoule, heated up to 1125 K for three days, and quenched at room temperature. In the heterogeneous mixture, some blue crystals were isolated on the alumina tube. The chemical composition $AlMoP_2O_9$ of these crystals was determined by microprobe analysis.

Table 2. Positional parameters and their estimated standard deviations.

Atom	x	y	z	B [Å^2]
Al	0.750	0.250	0.000	0.56(1)
Mo	0.250	0.250	0.17748(6)	0.445(3)
P	0.56514(9)	0.435	0.250	0.460(8)
O(1)	0.3929(2)	0.4141(2)	0.2332(3)	0.83(3)
O(2)	0.250	0.250	−0.0126(6)	1.22(4)
O(3)	0.6472(3)	0.3779(4)	0.1084(4)	1.38(4)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\ \{a^2 B_{11} + b^2 B_{22} + \ldots bc \cos \alpha B_{23}\}$.

Structure determination

A blue crystal of $0.072 \times 0.072 \times 0.060$ mm^3 has been chosen for the structure determination. The Laue patterns showed the symmetry $4/mmm$. The cell parameters reported in Table 1 were determined and refined by diffractometric techniques at 294 K with a least-squares refinement based on 25 reflections with $18 < \theta < 22°$. The data were collected on a CAD-4 Enraf-Nonius diffractometer. The reflections were corrected for Lorentz and polarization effects, no absorption corrections were performed. The atomic coordinates of the molybdenum, aluminium and phosphorus atoms were deduced from the Patterson function and the oxygen atoms were located by subsequent Fourier syntheses. A full-matrix least-squares refinement with a weighting scheme $w = f(\sin\theta/\lambda)$ adjusted using the program POND (Leclaire, unpublished) of the atomic coordinates and the anisotropic thermal factors lead to $R = 0.027$, $R_w = 0.031$ and to the coordinates listed in Table 2[1].

Description of the structure and discussion

These results show that this new phase $MoAlP_2O_9$ is isostructural with $VSiP_2O_9$ (Middelmiss and Calvo, 1976). However the replacement of silicon by aluminium leads to a much more open structure. The projections of the structure along $\vec{c}$ (Fig. 1) and along $\vec{a}$ (Fig. 2) allow a simple description of

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[1] Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 53522, the names of the authors and the title of the paper.

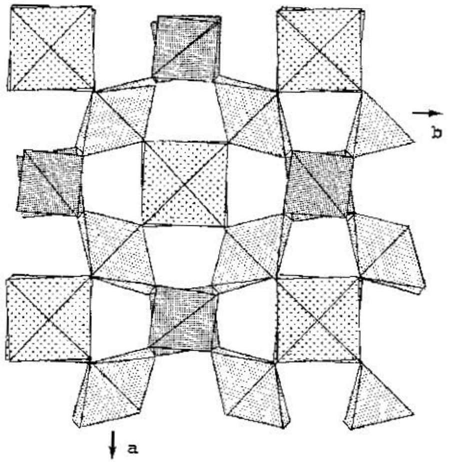

Fig. 1. Projection of the $MoAlP_2O_9$ structure along $\vec{c}$.

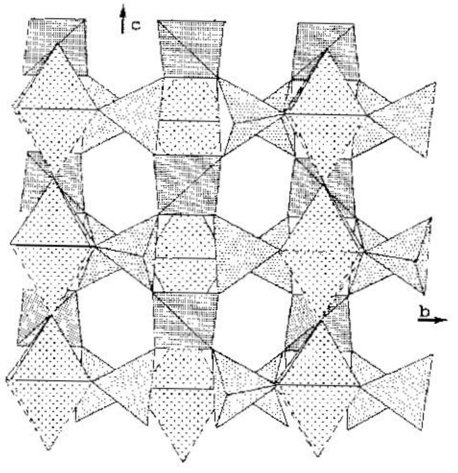

Fig. 2. Projection of the $MoAlP_2O_9$ structure along $\vec{a}$.

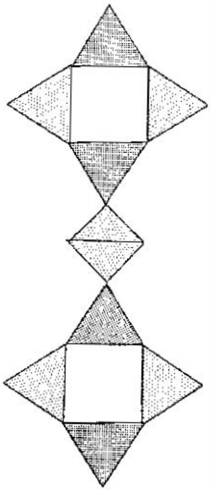

Fig. 3. The square windows in the $[AlP_2O_6]_\infty$ columns.

the structure to be proposed. One indeed observes infinite rows of MoO_6 octahedra running along $\vec{c}$ (Fig. 2); such ReO_3-type rows, which can be formulated $[MoO_3]_\infty$ are similar to those observed in $MoPO_5$ (Kierkegaard 1964) and α-VPO_5 (Jorden et al., 1973); another striking similarity with those compounds concerns the existence of $[MoPO_5]_\infty$ rows running along $\langle 110 \rangle$, in which one PO_4 tetrahedron alternates with one MoO_6 octahedron (Fig. 1). The second original feature of this structure deals with the existence of infinite columns of corner-sharing AlO_4 and PO_4 tetrahedra running along $\vec{c}$ (Fig. 1). Such columns which can be formulated $[AlP_2O_6]_\infty$ are built from one AlO_4 tetrahedron surrounded by four PO_4 tetrahedra and forming square windows (Fig. 3); along $\vec{c}$ the successive square windows are turned by 90° alternatively. Thus, the structure of $MoAlP_2O_9$ can be described as the assemblage of $[MoO_3]_\infty$ octahedral rows with $[AlP_2O_6]_\infty$ tetrahedral rows which share the corners of their MoO_6 octahedra and PO_4 octahedra, leading to the structural formula $(MoO_3)(AlP_2O_6)$.

The geometry of the MoO_6 octahedra is characteristic of that generally observed for molybdenum (V), i.e. very similar to those of Mo(V) in the α-$KMo_2P_3O_{13}$ (Leclaire, Monier and Raveau, 1983), β-$CsMo_2P_3O_{13}$ (Lii and Haushalter, 1987), γ-$CsMo_2P_3O_{13}$ (Chen et al., 1988) δ-$KMo_2P_3O_{13}$ (Leclaire et al., in the press) or $AgMo_5P_8O_{33}$ (Lii, Johnston, Goshorn and Haushalter, 1987) and $Mo_2P_4Si_4O_{23}$ (Leclaire et al., 1989). One observes a

Table 3. Distances (Å) and angles (°) in the MoO_6 octahedron.

Mo	O(1)	O(1^{i})	O(1^{ii})	O(1^{iii})	O(2)	O(2^{iv})
O(1)	1.976(2)	3.831(3)	2.709(3)	2.709(3)	2.870(5)	2.925(5)
O(1^{i})	151.6(2)	1.976(2)	2.709(3)	2.709(3)	2.870(5)	2.925(5)
O(1^{ii})	86.6(1)	86.6(1)	1.976(2)	3.31(3)	2.870(5)	2.925(5)
O(1^{iii})	86.6(1)	86.6(1)	151.6(2)	1.976(2)	2.870(5)	2.925(5)
O(2)	104.2(1)	104.2(1)	104.2(1)	104.2(1)	1.654(5)	4.349(5)
O(2^{iv})	75.8(1)	75.8(1)	75.8(1)	75.8(1)	180.00	2.695(5)

Symmetry code:

i:	1/2-x;	1/2-y;	z
ii:	1/2-y;	x;	z
iii:	y;	1/2-x;	z
iv:	1/2-x;	y;	1/2 + z
v:	3/2-x;	1/2-y;	z
vi:	y + 1/2;	1-x;	$-z$
vii:	1-y;	x-1/2;	$-z$
viii:	1-y;	1-x;	1/2-z
ix:	1/2-x;	y-1/2;	1/2 + z
x:	1-x;	1-y;	1-z
xi:	1-x;	y-1/2;	1-z
xii:	x + 1/2;	y;	1/2-z

Table 4. Distances (Å) and angles (°) in the AlO_4 tetrahedron.
Symmetry code see Table 3.

Al	O(3)	O(3^{v})	O(3^{vi})	O(3^{vii})
O(3)	1.725(3)	2.888(6)	2.779(5)	2.779(5)
O(3^{v})	113.8(2)	1.725(3)	2.779(5)	2.779(5)
O(3^{vi})	107.4(1)	107.4(1)	1.725(3)	2.888(6)
O(3^{vii})	107.4(1)	107.4(1)	113.8(2)	1.725(3)

very short Mo–O bond (1.654 Å) corresponding to a molybdenyl group, four medium ones (1.976 Å) and a very long one (2.695 Å) (Table 3). The "O_6" octahedron is almost regular (Table 3) but the O–Mo–O angles range from 75.8 to 104.2° due to the fact that the molybdenum atom is strongly off-centered by about 0.48 Å from the plane of the four oxygen atoms giving the medium Mo–O bonds. So one may also consider the molybdenum atom in a square pyramidal coordination. The stacking of these pyramids leads to a string of corner-sharing octahedra.

The AlO_4 tetrahedron is a little distorded in spite of its four identical Al–O bonds (Table 4). The PO_4 tetrahedron has the classical geometry observed in monophosphates (Table 5). One observes that the P–O bonds involving an oxygen atom common to Mo and P are a little longer than those involving oxygen atoms bridging aluminium and phosphorus atoms.

Table 5. Distances (Å) and angles (°) in the PO_4 tetrahedron. Symmetry code see Table 3.

P	O(1)	O(1^{viii})	O(3)	O(3^{viii})
O(1)	1.534(3)	2.420(4)	2.508(4)	2.502(4)
O(1^{viii})	104.2(2)	1.534(3)	2.502(4)	2.508(4)
O(3)	110.8(2)	110.4(2)	1.514(3)	2.483(7)
O(3^{viii})	110.4(2)	110.8(2)	110.2(3)	1.514(3)

Table of refined displacement parameter expressions — Beta's.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Al	0.00195(8)	B(1,1)	0.0015(1)	0	0	0
Mo	0.00092(1)	B(1,1)	0.00252(3)	0	0	0
P	0.00121(4)	B(1,1)	0.00208(8)	−0.0001(1)	−0.0003(1)	B(1,3)
O(1)	0.0015(2)	0.0018(2)	0.0050(2)	−0.0002(3)	−0.0010(4)	−0.0002(4)
O(2)	0.0045(3)	B(1,1)	0.0029(4)	0	0	0
O(3)	0.0039(2)	0.0048(3)	0.0048(3)	0.0011(4)	0.0028(5)	−0.0038(5)

The form of the anisotropic displacement parameter is: $\exp[-(B(1,1)*h2 + B(2,2)*k2 + B(3,3)*12 + B(1,2)*hk + B(1,3)*hl + B(2,3)*kl)]$.

As a conclusion, the synthesis of this new molybdenum aluminophosphate shows the ability of aluminium to participate in the formation of mixed frameworks built up from octahedra and tetrahedra. The fact that aluminium takes a tetrahedral coordination is of great importance for the edification of more open structures in this field.

References

Chen, J. J., Lii, K. H., Wang, S. L.: A new Mo^{5+} phosphate with a tunnel structure: $\gamma CsMo_2P_3O_{13}$. J. Solid State Chem. **76** (1988) 204–209.

Gopal, R., Calvo, C.: Crystal structure of βVPO_5. J. Solid State Chem. **5** (1972) 432–435.

Gorbunova, Y. E., Linde, S. A.: Structure of crystals of vanadyl pyrophosphate $(VO)_2P_2O_7$. Dokl. Akad. Nauk SSSR **245** (1979) 584–588.

Jordan, B., Calvo, C.: Crystal structure of α-vanadium holophosphate. Can. J. Chem. **51** (1973) 2621–2625.

Kierkegaard, P., Westerlund, M.: The crystal structure of $MoOPO_4$. Acta Chem. Scand. **18** (1964) 2217–2225.

Leclaire, A., Borel, M. M., Grandin, A., Raveau, B.: $Mo_2P_4Si_4O_{23}$, a molybdenum V silicophosphate related to the β cristobalite. J. Solid State Chem. **80** (1989) 250–255.

Leclaire, A., Borel, M. M., Grandin, A., Raveau, B.: Crystal structure of a molybdenum V phosphate: $\beta KMo_2P_3O_{13}$. Acta Crystallogr., in press.

Leclaire, A., Borel, M. M., Grandin, A., Raveau, B.: A novel form of molybdenum V phosphate: $\delta KMo_2P_3O_{13}$. Z. Kristallogr. **188** (1989) 77–83.

Leclaire, A., Monier, J. C., Raveau, B.: $K_4Mo_8^VP_{12}O_{52}$. A tunnel structure characterized by an unusual valence of molybdenum. J. Solid State Chem. **48** (1983) 147–153.

Lii, K. H., Johnston, D. C., Goshorn, D. P., Haushalter, R. C.: Crystal structure and magnetic properties of a new molybdenophosphate: $AgMo_5P_8O_{33}$. J. Solid State Chem. **71** (1987) 131–138.

Lii, K. H., Haushalter, R. C.: Layer and tunnel structures is new molybdenophosphates: $Cs_2Mo_4P_6O_{26}$ and $M_4Mo_8P_{12}O_{52}$ (M = Cs, Rb, K, Tl). J. Solid State Chem. **69** (1987) 320–328.

Middelmiss, N., Calvo, C.: Oxovanadium (IV) diphosphatomonosilicate. Acta Crystallogr. **B32** (1976) 2826–2898.