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# $Mo_2P_4Si_4O_{23}$, a Molybdenum (V) Silicophosphate Related to the $\beta$-Cristobalite

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Single crystals of a new molybdenum (V) silicophosphate $Mo_2P_4Si_4O_{23}$ have been synthesized and studied by X-ray diffraction. This compound crystallizes in the space group $P\bar{1}$ with $a = 8.415(2)$, $b = 5.215(2)$, $c = 11.190(1)$ Å, $\alpha = 77.77(2)$, $\beta = 77.77(1)$, $\gamma = 73.11(2)°$. The structure is formed of corner-sharing $MoO_6$ octahedra, $PO_4$ tetrahedra, and $SiO_4$ tetrahedra. It can be described as built up from $[P_4Si_4O_{16}]_\infty$ $\beta$-cristobalite-type layers parallel to (001) connected through $[Mo_2O_7]_\infty$ planes of $MoO_6$ octahedra. Such a compound suggests the possibility of generating different members, $[P_4Si_{4+m}O_{16+2m}][Mo_2O_7]$, differing from each other only by the thickness of the $\beta$-cristobalite layer, i.e., by the number of $SiO_4$ tetrahedra. © 1989 Academic Press, Inc.

## Introduction

The different investigations of oxides involving phosphorus and molybdenum have shown an extraordinarily rich crystal chemistry since about 20 phosphates of molybdenum have been isolated, whose mixed framework is built up of $MoO_6$ octahedra and $PO_4$ tetrahedra, and characterized by various oxidation states of molybdenum ranging from Mo(III) to Mo(VI) (*1–21*). Although not too numerous, several silicophosphates of molybdenum have recently been isolated. These latter oxides—$AMo_3P_6Si_2O_{25}$, $A$ = K, Rb, Tl, Cs (*22–24*); $Mo_4P_6Si_2O_{25}$ (*25*); $MoP_3SiO_{11}$ (*26*); $Mo_3P_5SiO_{19}$ (*27*)—have a common structural feature: their host lattice is characterized by the presence of the same structural unit "$P_6Si_2O_{25}$" formed of a disilicate group sharing its corners with six $PO_4$ tetrahedra. During the investigation of one of those system Ag–Mo–P–Si–O crystals of a new phase, involving Mo(V), $Mo_2P_4Si_4O_{23}$ were isolated. We report here on the crystal structure of this compound which is closely related to $\beta$-cristobalite.

## Experimental

A reaction aiming at "$AgMo_2P_3O_{12}$" was performed in two steps. First an adequate mixture of $Ag_2CO_3$, $H(NH_4)_2PO_4$, and $MoO_3$ was heated to 673 K in order to eliminate $CO_2$, $H_2O$, and $NH_3$. In the second step the resulting finely ground product was mixed with an appropriate amount of molybdenum and sealed in an evacuated silica ampoule. This sample was then heated up to 1073 K for 2 days and quenched at room temperature. When the ampoule was opened we obtained a mixture in which some green transparent plate crystals were isolated. The composition deduced from

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TABLE I

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT PARAMETERS FOR $Mo_2P_4Si_4O_{23}$

| | | |
|---|---|---|
| | 1. Crystal data | |
| Space group | $P\bar{1}$ | |
| Cell dimensions | $a = 8.415(1)$ Å | $\alpha = 77.77(2)^\circ$ |
| | $b = 5.215(2)$ | $\beta = 77.77(1)$ |
| | $c = 11.190(1)$ | $\gamma = 73.11(2)$ |
| Volume | $V = 453.3(2)$ Å$^3$ | |
| $Z$ | 1 | |
| | 2. Intensity measurement | |
| $\lambda$ (Mo$K\bar{\alpha}$) | 0.71073 Å | |
| Scan mode | $\omega$-$\frac{2}{3}\theta$ | |
| Scan width (°) | $1.1 + 0.35 \tan \theta$ | |
| Slit aperture (mm) | $1. + \tan \theta$ | |
| Max $\theta$ (°) | 45 | |
| Standard reflections | 3 measured every 2000 sec (no decay) | |
| Reflections with $I > 3\sigma$ | 1263 | |
| | 3. Structure solution and refinement | |
| Parameters refined | 151 | |
| Agreement factors | $R = 0.043$, $R_w = 0.048$ | |

the structural determination, $Mo_2P_4Si_4O_{23}$, was confirmed by microprobe analysis. Subsequently a reaction to prepare pure $Mo_2P_4Si_4O_{23}$ was performed but we could not obtain this phase in this manner.

## Structure Determination

A green plate crystal with dimensions $0.216 \times 0.024 \times 0.012$ mm was selected for the structure determination. The cell parameters reported in Table I were determined and refined by diffractometric techniques at 294 K with a least-squares refinement based upon 25 reflections with $18 < \theta < 22^\circ$.

The data were collected on a CAD-4 Enraf–Nonius diffractometer with the data collection parameters reported in Table I. The reflections were corrected for Lorentz and polarization effects; no absorption corrections were performed.

Atomic coordinates of the molybdenum atom were deduced from the Patterson function and the other atoms were located by subsequent Fourier series. Refinement of the atomic coordinates and their anisotropic thermal parameters led to $R = 0.043$, $R_w = 0.048$ and to the atomic parameters of Table II.

## Description of the Structure and Discussion

The structure of $Mo_2P_4Si_4O_{23}$ (Fig. 1) is built up from corner-sharing $MoO_6$ octahedra and $PO_4$ and $SiO_4$ tetrahedra.

Each $MoO_6$ octahedra shares five corners with a $PO_4$ tetrahedron, whereas the sixth corner is free. The "$O_6$" octahedron is almost regular, but Mo is off-centered. It results in four medium Mo–O distances (1.998 to 2.053 Å), a longer one (2.119 Å), and a very short one (1.661 Å), as shown in Table III. This geometry and especially the short Mo–O distance corresponding to the free oxygen is characteristic of Mo(V) and has already been observed in other Mo(V) phosphates: $K_4Mo_8P_{12}O_{52}$ (*11*), $Cs_2Mo_4$

TABLE II

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

| Atom | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| Mo | 0.2544(1) | 0.2910(2) | 0.14829(8) | 0.69(1) |
| P(1) | 0.3147(3) | −0.1585(4) | −0.0528(2) | 0.71(4) |
| P(2) | 0.1891(3) | 0.7510(4) | 0.3317(2) | 0.67(3) |
| Si(1) | 0.3130(3) | 0.5584(5) | 0.5722(2) | 0.71(4) |
| Si(2) | −0.1870(3) | −0.0574(5) | 0.2863(2) | 0.68(4) |
| O(1) | 0.2551(8) | −0.001(1) | 0.3031(6) | 1.2(1) |
| O(2) | 0.3037(9) | 0.548(1) | −0.0059(6) | 1.3(1) |
| O(3) | 0.2627(9) | 0.002(1) | 0.0528(6) | 1.1(1) |
| O(4) | 0.2892(8) | 0.532(1) | 0.2587(6) | 1.1(1) |
| O(5) | 0.0462(9) | 0.408(1) | 0.1699(7) | 1.6(1) |
| O(6) | 0.5194(8) | 0.143(1) | 0.1318(6) | 1.3(1) |
| O(7) | 0.1737(8) | −0.028(1) | −0.1379(6) | 1.2(1) |
| O(8) | 0.1837(8) | 0.638(1) | 0.4728(6) | 1.1(1) |
| O(9) | 0.0020(8) | −0.174(2) | 0.3165(7) | 1.5(1) |
| O(10) | −0.2808(9) | −0.294(1) | 0.3368(6) | 1.5(1) |
| O(11) | −0.2800(9) | 0.198(1) | 0.3539(7) | 1.7(1) |
| O(12) | 0.500 | 0.500 | 0.500 | 1.3(2) |

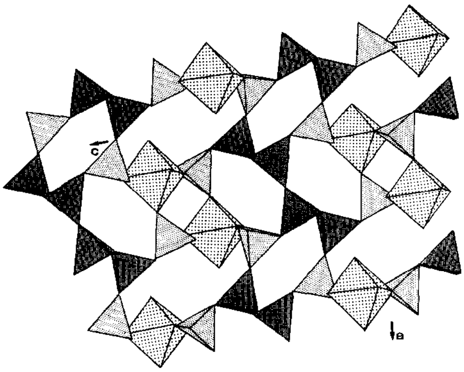

FIG. 1. Projection of the structure of $Mo_2P_4Si_4O_{23}$ along **b**.

$P_6O_{26}$ (*12*), γ-$CsMo_2P_3O_{13}$ (*13*), and δ-$KMo_2P_3O_{13}$ (*14*).

Two types of $PO_4$ tetrahedra are observed. Each P(1) tetrahedron shares three corners with three $MoO_6$ octahedra and the fourth corner with a $SiO_4$ tetrahedron. Each P(2) tetrahedron is linked to two $MoO_6$ octahedra and two $SiO_4$ tetrahedra. The P–O distances are rather homogeneous, ranging from 1.49 to 1.585 Å (Table IV). However, it must be pointed out that the P–O distances involving oxygen atoms common to Mo and P are shorter than those corresponding to the P–O–Si bonds, in agreement with the distances previously observed in the silicophosphates $AMo_3P_6Si_2O_{25}$ (*22–24*), $Mo_4P_6Si_2O_{25}$ (*25*), and $MoP_3SiO_{11}$ (*26*).

TABLE III

DISTANCES IN (Å) AND ANGLES (°) IN THE $MoO_6$ OCTAHEDRON

| Mo | O(1) | O(2) | O(3) | O(4) | O(5) | O(6) |
|---|---|---|---|---|---|---|
| O(1) | 2.051(8) | 4.03(1) | 2.79(1) | 2.81(1) | 2.73(1) | 2.78(1) |
| O(2) | 168.5(3) | 1.998(8) | 2.89(1) | 2.92(1) | 2.76(1) | 2.78(1) |
| O(3) | 86.8(3) | 92.6(3) | 2.002(7) | 4.03(1) | 2.73(1) | 2.83(1) |
| O(4) | 86.3(3) | 92.3(3) | 168.2(3) | 2.053(8) | 2.74(1) | 2.77(1) |
| O(5) | 94.1(4) | 97.4(4) | 95.8(4) | 94.3(4) | 1.661(9) | 3.78(1) |
| O(6) | 83.7(3) | 84.8(3) | 86.6(3) | 83.1(3) | 176.6(4) | 2.119(8) |

TABLE IV

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

| P(1) | O(2$^{i}$) | O(3) | O(6$^{ii}$) | O(7) |
|---|---|---|---|---|
| O(2$^{i}$) | 1.530(8) | 2.50(1) | 2.52(1) | 2.48(1) |
| O(3) | 110.5(5) | 1.508(8) | 2.54(1) | 2.46(1) |
| O(6$^{ii}$) | 112.3(5) | 115.2(5) | 1.501(8) | 2.49(1) |
| O(7) | 105.6(5) | 105.0(5) | 107.4(4) | 1.585(8) |
| **P(2)** | **O(1$^{iii}$)** | **O(4)** | **O(8)** | **O(9$^{iii}$)** |
| O(1$^{iii}$) | 1.499(8) | 2.51(1) | 2.48(1) | 2.51(1) |
| O(4) | 114.1(5) | 1.493(8) | 2.49(1) | 2.49(1) |
| O(8) | 108.5(4) | 109.4(5) | 1.559(8) | 2.43(1) |
| O(9$^{iii}$) | 111.0(5) | 110.3(5) | 102.9(5) | 1.545(8) |

*Note*. For symmetry code, see Table 5.

Two types of $SiO_4$ tetrahedra are also involved in this structure. In the Si(1) tetrahedron, three corners are shared with Si tetrahedra and one corner with a $PO_4$ tetrahedron, whereas in the Si(2) tetrahedron two corners are shared with Si(1) tetrahedra and two corners with $PO_4$ tetrahedra. In the same way as noticed above for $PO_4$ tetrahedra, the Si–O distances (Table V) corresponding to the Si–O–Si bonds are

TABLE V

DISTANCES (Å) AND ANGLES (°) IN THE $SiO_4$ TETRAHEDRA

| Si(1) | O(8) | O(10$^{iv}$) | O(11$^{v}$) | O(12) |
|---|---|---|---|---|
| O(8) | 1.628(9) | 2.59(1) | 2.63(1) | 2.61(1) |
| O(10$^{iv}$) | 107.1(4) | 1.588(9) | 2.62(1) | 2.61(1) |
| O(11$^{v}$) | 109.9(5) | 111.0(5) | 1.588(9) | 2.59(1) |
| O(12) | 108.9(3) | 110.5(4) | 109.4(4) | 1.584(3) |
| **Si(2)** | **O(7$^{vi}$)** | **O(9)** | **O(10)** | **O(11)** |
| O(7$^{vi}$) | 1.614(8) | 2.60(1) | 2.65(1) | 2.64(1) |
| O(9) | 107.3(4) | 1.610(8) | 2.58(1) | 2.61(1) |
| O(10) | 111.4(4) | 107.5(5) | 1.593(9) | 2.61(1) |
| O(11) | 110.9(5) | 109.3(5) | 110.3(5) | 1.588(9) |

*Note*. Symmetry code: i, $x$, $y - 1$, $z$; ii, $1 - x$, $-y$, $-z$; iii, $x$, $1 + y$, $z$; iv, $-x$, $-y$, $1 - z$; v, $-x$, $1 - y$, $1 - z$; vi, $-x$, $-y$, $-z$.

TABLE VI

Refined Displacement Parameter Expressions $\beta$'s

| Name | $\beta$ (1,1) | $\beta$ (2,2) | $\beta$ (3,3) | $\beta$ (1,2) | $\beta$ (1,3) | $\beta$ (2,3) |
|---|---|---|---|---|---|---|
| Mo | 0.00294(7) | 0.0080(2) | 0.00106(3) | −0.0012(2) | −0.00018(8) | −0.0019(1) |
| P(1) | 0.0032(2) | 0.0075(6) | 0.0014(1) | −0.0025(6) | −0.0015(3) | −0.0003(5) |
| P(2) | 0.0026(2) | 0.0085(6) | 0.0010(1) | −0.0016(6) | −0.0007(3) | −0.0005(5) |
| Si(1) | 0.0028(3) | 0.0077(7) | 0.0013(1) | −0.0014(7) | 0.0004(3) | −0.0022(5) |
| Si(2) | 0.0025(3) | 0.0080(7) | 0.0012(1) | 0.0004(7) | −0.0015(3) | −0.008(5) |
| O(1) | 0.0069(8) | 0.011(2) | 0.0020(4) | −0.005(2) | −0.003(1) | −0.001(1) |
| O(2) | 0.0064(9) | 0.007(2) | 0.0029(5) | −0.002(2) | −0.001(1) | −0.003(2) |
| O(3) | 0.0077(9) | 0.007(2) | 0.0024(4) | −0.005(2) | −0.001(1) | −0.006(1) |
| O(4) | 0.0047(8) | 0.008(2) | 0.0031(4) | 0.001(2) | −0.003(1) | −0.004(2) |
| O(5) | 0.0054(8) | 0.018(2) | 0.0042(5) | −0.003(2) | −0.004(1) | −0.008(2) |
| O(6) | 0.0030(8) | 0.016(2) | 0.0023(5) | 0.000(2) | −0.001(1) | 0.002(2) |
| O(7) | 0.0023(7) | 0.020(2) | 0.0012(4) | −0.000(2) | −0.0015(9) | 0.003(2) |
| O(8) | 0.0045(8) | 0.017(2) | 0.0016(4) | −0.012(2) | 0.0004(9) | 0.001(2) |
| O(9) | 0.0033(7) | 0.022(3) | 0.0028(4) | 0.001(2) | −0.0045(9) | −0.000(2) |
| O(10) | 0.006(1) | 0.014(2) | 0.0028(5) | −0.001(3) | −0.003(1) | 0.004(2) |
| O(11) | 0.006(1) | 0.017(2) | 0.0044(5) | 0.005(3) | −0.003(1) | −0.014(1) |
| O(12) | 0.001(1) | 0.026(4) | 0.0014(6) | −0.002(3) | 0.001(1) | −0.001(3) |

*Note*. The form of the anisotropic displacement parameter is: $\exp[-(\beta(1,1)*h2 + \beta(2,2)*k2 + \beta(3,3)*l2 + \beta(1,2)*hk + \beta(1,3)*hl + \beta(2,3)*kl$.

shorter than those corresponding to the Si–O–P bonds, as observed for other silicophosphates of molybdenum (*22–26*). (For the refined displacement parameter expressions of $\beta$ see Table VI.)

The examination of the structure along the [100] direction (Fig. 2a) shows that it is closely related to that of $\beta$-cristobalite (*28, 29*) (Fig. 2b). It consists indeed of $\beta$-cristobalite layers parallel to the ($a$,$c$) plane and connected to each other through $MoO_6$ octahedra. Such layers are four tetrahedra thick, i.e., formed of strings of four tetrahedra running along $c$; in these chains, the two $SiO_4$ tetrahedra are located inside the layers, whereas the two $PO_4$ tetrahedra are

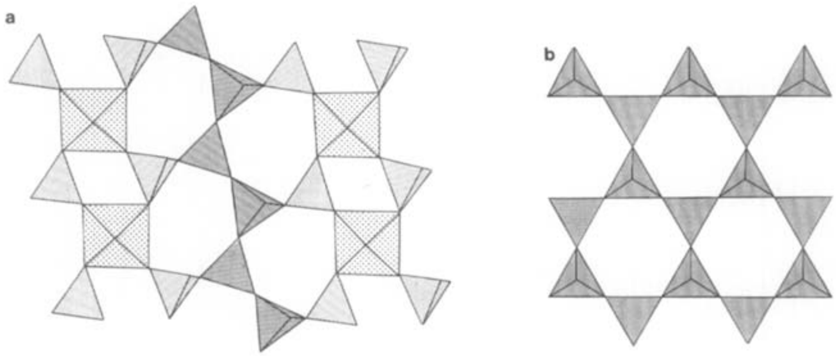

Fig. 2. (a) Partial projection of the structure on (100) showing the $\beta$-cristobalite slices. (b) Partial projection of the $\beta$-cristobalite along [111].

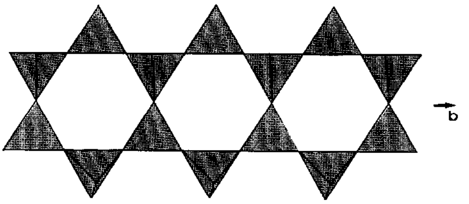

FIG. 3. The $[Si_4O_8)_\infty$ ribbon running along **b**.

located on the side of the layer, i.e. are connected to the $MoO_6$ octahedra. The segregation of the $SiO_4$ tetrahedra in the layers can be seen in Fig. 3: the $SiO_4$ tetrahedra form infinite ribbons $[Si_4O_8]_\infty$ running along the *b* axis. In these ribbons, one can distinguish the hexagonal rings built up of six tetrahedra, which are characteristic of the $\beta$-cristobalite. Thus the structure of this phase can be described in terms of $[P_4Si_4O_{16}]_\infty$ $\beta$-cristobalite-type layers parallel to (001) connected through octahedral planes $[Mo_2O_7]_\infty$ in which the $MoO_6$ octahedra are disconnected from each other. This description shows that the possibility of the existence of different members $(P_4Si_{4+m}O_{16+2m})(Mo_2O_7)$, corresponding to various thicknesses of the $\beta$-cristobalite layers, should be considered.

It is also worth noting that there exists in the structure infinite ribbons $[P_4Mo_2O_{15}]_\infty$ running along *b* also forming hexagonal rings built up from three $MoO_6$ octahedra and three $PO_4$ tetrahedra (Fig. 4) so that the structure of this phase can also be described by the assemblage of $[Si_4O_8]_\infty$ ribbons and $[P_4Mo_2O_{15}]_\infty$ ribbons.

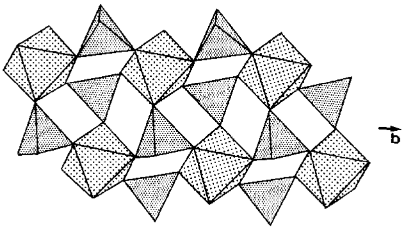

FIG. 4. The $[Mo_2P_4O_{15}]_\infty$ ribbon running along **b**.

This structure can also be compared to that of the phosphate $NaTiP_2O_7$ (*30*) which is formed of $\beta$-cristobalite layers connected through single slabs of octahedra. Thus from these studies, it appears that the $\beta$-cristobalite is a rather flexible structure which can adapt octahedra, opening a route to the synthesis of new structural families.

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