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Determination of the crystal structure of $Mo^{V}_2P_4O_{15}$

G. Costentin, A. Leclaire, M. M. Borel, A. Grandin and B. Raveau

Laboratoire de Cristallographie et Sciences des Matériaux, Crismat, Ismra,
Boulevard du Maréchal Juin, 14050 Caen Cedex, France

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Abstract. The structure of a molybdenum tetraphosphate $Mo_2P_4O_{15}$ has been determined from X-ray single crystal study in the monoclinic space group $P2_1/c$ ($a = 8.3068(8)$, $b = 6.5262(6)$, $c = 10.718(1)$ Å, $\beta = 106.70(1)°$). Its structure consists of MoO_6 octahedra sharing five of their corners with P_4O_{13} tetraphosphate groups, the sixth one being free corresponds to a molybdenyl group.

Introduction

A great variety of molybdenum phosphates have been observed, whose frameworks consist of corner-sharing MoO_6 octahedra and PO_4 tetrahedra. Their recent study has shown the great ability of the phosphate matrix to stabilize the pentavalent state of molybdenum as in $MoPO_5$ (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., 1990), $CsMo_2P_3O_{13}$ (Lii and Haushalter, 1987; Chen et al., 1988), $AgMo_5P_8O_{33}$ (Lii, Johnston, Goshorn and Haushalter, 1987), $BaMo_2P_4O_{16}$ and ζ$NaMo_2P_3O_{13}$ (Costentin et al., 1990).

In an attempt to prepare new members of the Mo(V) phosphates family, the investigation of the system Mg–Mo–P–O was undertaken. During this study, several crystals of the oxide $Mo_2P_4O_{15}$ were isolated. We noticed that the space group and cell parameters were different from those published by Minacheva et al. (1979). We report here on the crystal structure of this Mo(V) phosphate.

Table 1. Summary of crystal data, intensity measurements and structure refinement parameters for $Mo_2P_4O_{15}$.

1° – Crystal data:	
Space group	$P2_1/c$
Cell dimensions	$a = 8.3068(8)$ Å
	$b = 6.5262(6)$ Å; $\beta = 106.7051(78)°$
	$c = 10.7181(11)$ Å
Volume	$V = 556(1)$ Å^3
Z	2
2° – Intensity measurements:	
$\lambda(MoK\alpha)$	0.71073 Å
Scan mode	ω-θ
Scan width (°)	$0.80 + 0.35 \tan\theta$
Slit aperture (mm)	$1 + \tan\theta$
Max θ (°)	45
Standard reflections	3 measured every 3000 s (no decay)
Reflections with $I > 3\sigma$	408
Absorption μ(mm^{-1})	2.86
3° – Structure solution and refinement:	
Parameters refined	100
Agreement factors	$R = 0.036$
	$Rw = 0.037$
Weighting scheme	$W = f(\sin\theta/\lambda)$
Δ/σ max	0.03
$d\rho$ max	0.970 e/Å^3

Experimental

In our attempt to prepare a phase of composition $Mg_{0.5}Mo_2P_3O_{13}$, the reaction was performed in two steps.

First an adequate mixture of $MgCO_3$, $H(NH_4)_2PO_4$, MoO_3 was heated to 873 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 four days. When the ampoule was opened, we obtained a mixture in which some green plate crystals were isolated. The composition deduced from the structural determination $Mo_2P_4O_{15}$ was confirmed by microprobe analysis. Subsequently, a reaction to prepare pure $Mo_2P_4O_{15}$ was performed. The powder X-ray diffraction pattern of the phase was indexed in a monoclinic cell, in agreement with the parameters obtained from the single crystal study (Table 1).

It is worth pointing out that this phase differs from that described by Minacheva et al. (1979), by the size of its cell, due to the b value (6.52 Å) which is three times smaller than that observed by these authors (19.52 Å), leading, of course, to a different space group $P2_1/c$ instead of Pb.

Table 2. Positional parameters and their estimated standard deviations.

Atom	x	y	z	B
Mo	0.2022(1)	0.2547(5)	0.1496(1)	2.03(2)
P(1)	0.1845(5)	0.5559(7)	0.3988(5)	2.14(9)
P(2)	0.4159(4)	0.8868(8)	0.3737(4)	2.0(1)
O(1)	0.150(1)	0.436(3)	0.044(2)	8.9(4)
O(2)	0.451(1)	0.299(2)	0.177(1)	3.7(4)
O(3)	0.202(2)	0.022(3)	0.028(1)	7.3(5)
O(4)	−0.027(1)	0.172(2)	0.155(1)	4.8(4)
O(5)	0.225(2)	0.414(3)	0.313(2)	10.0(5)
O(6)	0.289(1)	0.012(2)	0.287(1)	5.6(4)
O(7)	0.331(1)	0.715(3)	0.432(1)	6.8(4)
O(8)	0.486(3)	0.060(4)	0.476(2)	2.6(6)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$$B = \frac{4}{3}\sum_i\sum_j a_i \cdot a_j \cdot \beta_{ij}.$$

Structure determination

A green plate crystal with dimensions $0.051 \times 0.038 \times 0.032$ mm was selected for the structure determination. The cell parameters reported in Table 2 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 collection parameters reported in Table 1. 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. The Fourier difference synthesis showed that the O(8) oxygen was not located on the symmetry centre, but was statistically distributed over the general position 0.49, 0.06, 0.48, with an occupancy factor 0.5. Refinement of the atomic coordinates and their anisotropic thermal parameters led to $R = 0.036$, $Rw = 0.037$ and to the atomic parameters given in Table 2. The high values of isotropic B factors especially for several oxygen atoms (O(1), O(5), O(6) and (O7) led us to refine the anisotropic factors. The abnormally large anisotropic thermal factors suggest another space group. Attemps to refine the structure in the non-centro-symmetrical space group

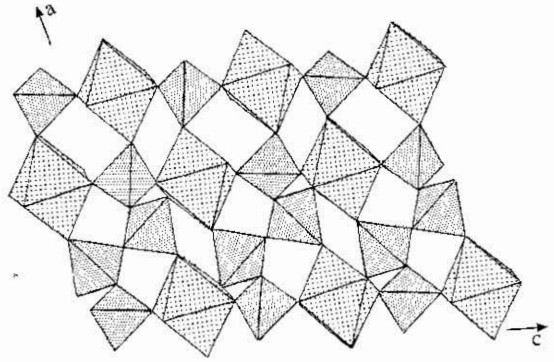

Fig. 1. Projection of $Mo_2P_4O_{15}$ along $\vec{b}$.

Pc, assuming that $0k0$ extinctions are also fortuitous were performed to avoid the statistical O(8) atom and the large thermal factors of other atoms. The refinements were unsuccessfull and correlations between the centrosymmetrical atoms in the $P2_1/c$ group were found equal to one. Then, the splitting of atoms on two neighbouring sites was undertaken in the $P2_1/c$ group, without any success, two initially splitted sites converging into a unique site. In order to detect additional reflections, a second data collection was undertaken using Cu*Kα* radiation and doubling the cell parameters. All the *hkl* reflections with $I > 2\sigma(I)$, correspond to $h, k, l = 2n$. Thus, neither superstructure reflections nor satellites were observed on the Weissenberg films. Consequently, we can admit that the structure is characterized by a dynamic disordered framework.[1]

Description of the structure and discussion

The structure of $Mo_2P_4O_{15}$ seems to be similar to that obtained by Minacheva et al. (1979). Unfortunately, these authors published only a (100) projection of the structure without any atomic coordinates and any bond length, so that a comparison of the two results is impossible.

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[1] Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Please quote reference no. CSD 55508, the names of the authors and the title of the paper.

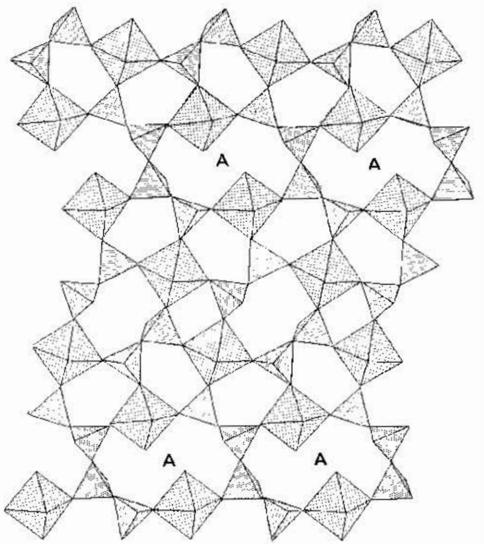

Fig. 2. $[Mo_2P_4O_{15}]$ layers parallel to [012].

The view of the structure along $\vec{b}$ (Fig. 1) shows that the three-dimensional $[Mo_2P_4O_{15}]_\infty$ framework consists of isolated MoO_6 octahedra, which share five of their corners with PO_4 tetrahedra and have one free corner, and of tetraphosphate groups, i.e. "P_4O_{13}" units, which share their ten apices with MoO_6 octahedra. The geometry of MoO_6 octahedra is characteristic of Mo(V); as observed in other Mo(V) phosphates, the "O_6" octahedra is rather regular, whereas Mo(V) is off centered; one observes an abnormally short Mo–O distance corresponding to the free corner of the octahedra, and one very long Mo–O bond, the four other Mo–O distances being normal. In the "P_4O_{13}" units, the shorter P–O distances correspond to P–O–Mo bonds, whereas the larger ones correspond to oxygen bridging to two phosphorous atoms. The O P O angles are close to 110°, whereas the P–O–P angles of the "O–P–O–P–O–P–O–P–O" chains range from 143° to 146°.

This structure can be described as the assemblage of infinite $[MoP_2O_{11}]_\infty$ chains running along $\vec{a}$ (Fig. 1), in which one P_2O_7 group alternates with one MoO_6 octahedron. Two successive chains share the corners of their polyhedra forming "P_4O_{13}" units running along the [$\bar{1}10$] directions.

This three-dimensional framework can also be described by the stacking of the identical [$Mo_2P_4O_{15})_\infty$ layers along the [$\bar{1}22$] direction parallel to (012) (Fig. 2). Such layers which consist of corner-sharing MoO_6 octahedra, P_2O_7 groups and P_4O_{13} units form three sorts of rings which can be compared to those observed in other phosphate tungsten bronzes. One indeed observes four-sided rings built up from two MoO_6 octahedra and two PO_4 tetrahedra like in $K_xP_2W_4O_{16}$ (Giroult et al., 1982), five-sided rings built up from two MoO_6 octahedra, one P_2O_7 group and one PO_4 tetrahedron to be compared to the pentagonal tunnels of the bronze $(PO_2)_4(WO_3)_{2m}$ (Labbé et al., 1986), and six-sided rings involving two MoO_6 octahedra and two P_2O_7 groups like in $P_8W_{12}O_{52}$ (Domenges et al., 1982). Note that in those planes the O – O distance between the free oxygen atoms of two adjacent MoO_6 octahedra is equal to 2.55 Å, so that the large rings labelled A can be described as the association of six-sided rings built up from three corner sharing tetrahedra and two MoO_6 octahedra.

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